Retrospective Theses and Dissertations

Iowa State University Capstones, Theses and Dissertations

1969

Electron spin resonance studies of some o-naphthosemiquinones and cyclic unsaturated semidiones

Kathleen Desmond Trahanovsky

Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Organic Chemistry Commons

70-13,641

TRAHANOVSKY, Kathleen Desmond, 1939-
ELECTRON SPIN RESONANCE STUDIES OF SOME o-
NAPHTHOSEMIQUINONES AND CYCLIC UNSATURATED
SEMIDIONES.

Iowa State University, Ph.D., 1969
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

ELECTRON SPIN RESONANCE STUDIES OF SOME o-NAPHTHOSEMIQUINONES

AND CYCLIC UNSATURATED SEMIDIONES

by

Kathleen Desmond Trahanovsky

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa
1969

TABLE OF CONTENTS

INTRODUCTION

The radical anion of an $\underline{\alpha}$-dicarbonyl compound is a paramagnetic species observable by electron spin resonance (esr) and may be used as a so-called "spin label." In aliphatic systems compounds containing this group are referred to as semi-diones; in aromatic systems they are called $\underline{o}$-semi-quinones. The unpaired electron is not restricted to the functional group but may be distributed through the remainder of the molecule. The hyperfine splitting constants (hfsc) obtained from esr spectra are a measure of unpaired spin density at various positions. In aromatic compounds the unpaired electron will be delocalized throughout the conjugated system. In non-aromatic systems the distribution is largely a function of geometry, which controls the extent to which the orbital with the unpaired electron can interact with orbitals on neighboring atoms. The greatest interaction is seen at adjacent positions and the hfsc of hydrogens attached to these sites are related to the dihedral angles between the orbitals containing the unpaired electron and the carbon-hydrogen bonds. Knowledge of these angles gives information about the conformational properties of molecules.

Esr studies of several flexible ring systems have been reported by Russell and Strom (1) for semidiones generated by reactions of the following type:
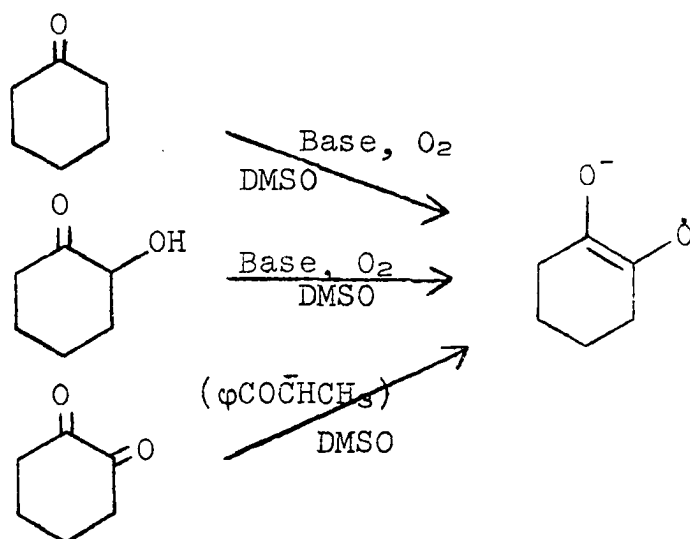
Conformational studies of these systems have been extended by variable temperature experiments leading to activation parameters and information as to population of various conformations in four to seven membered rings (2). In the case of unsymmetrically substituted ketones, or those in multiple ring systems, analysis of the spectra of the semidiones formed gives an indication of the structure and reactivity of the starting ketone. Successful applications of this aspect of esr work have been made to decalones and steroidal ketones (3). Long range interactions in more rigid bicyclic compounds have also been studied extensively (4).

Conversion of a saturated ketone to a semidione introduces one site of unsaturation into the ring so that stereochemical information obtained applies to the cyclic mono-olefin. If one or more double bonds were present in the initial ketone

elucidation of the conformations of poly-unsaturated ring systems would be possible. This would be of most interest for medium size rings. Similarly, benzo-ketones have an additional degree of unsaturation resulting in related stereochemical modifications. However, introduction of double bonds or aromatic rings raises additional problems in generating semidiones. Added reactivity due to double bonds and allylic and benzylic positions appears to make direct oxidation unfeasible and the diketones and hydroxy-ketones much less readily accessible. In the present study attempts to produce some cyclic unsaturated semidiones are reported.

Unsaturated ketones appear to react with oxygen in such a way that products result which do not give stable radical species under the conditions employed. Fragmentation is possible since oxidative cleavage is one of the common reactions of double bonds. Condensation or polymerization in the strongly basic media used is another probable complication. The inertness of the aromatic ring makes these competing processes less bothersome with benzo-derivatives. In these systems it is the highly reactive benzylic positions that are usually involved in further oxidation but the products of these oxidations are sometimes species which form stable radicals observable by esr. This is especially true where six-membered rings are present, since the products are quinones

which give highly stabilized semiquinone ions. Both α- and β-tetralone, for example, oxidize in basic solution to 2-hydroxy-1,4-naphthoquinone (lawsone) (5). The presumed intermediate is o-naphthoquinone. Use of this reaction to prepare lawsones

$$\xrightarrow{B^-,O_2} \qquad \xrightarrow{B^-,O_2}$$
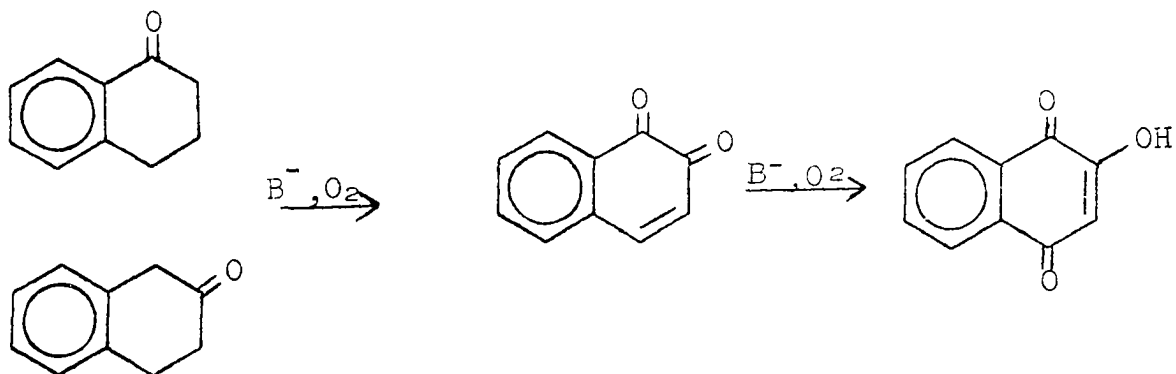
substituted in the benzene ring (6) is considerably more convenient than previously reported methods involving condensation of an α-tetralone with two moles of an amine followed by acid hydrolysis (7).

It has now become possible to observe these conversions and intermediates directly by esr. Since several substituted tetralones are available it has also been possible to use these to label specific positions in the quinone and thus to assign the splittings in the esr spectra to specific protons. This has not previously been done for o-naphthoquinone itself, although esr signals have been observed from this compound. In a table of esr results from oxidation of several compounds, o-naphthoquinone was reported to give a 17 line spectrum,

the same as that obtained from oxidation of β-naphthol (8).
These radicals were generated in alkaline water, ethanol or
acetone, and their spectra showed spacings of 1.3 and 0.24
gauss. No more detailed analysis was offered in the text.
Calculations by some Japanese workers predicted a doublet of
4.5 gauss but no experimental verification was attempted (9).

Much interest has centered on quinones as models for
molecular orbital calculations of delocalization energies and
spin densities, where the results can be compared with data
from esr spectra of the related radical ions. Splitting
constants and their assignments based on Huckel and McLachlan
molecular orbital treatments have been reported for several
semiquinones by Fraenkel and his coworkers, (10, 11) and by
Bersohn (12). These resulted in satisfactory agreement for
several 1,4-quinones, but only phenanthrenequinone in the
1,2-series was included. Brandon and Lucken have pointed out
in a similar study that explanation of spectra from o-semi-
quinones required a variety of sets of coulomb and resonance
integral parameters, none of which corresponded to the unique
set of values which explained available data for p-quinones
(13).

Part of this confusion may arise from the fact that better
spectral data are available for the p-quinones since they are
more stable to further oxidation than the o-quinones, which

are so easily oxidized that more than one spectrum can be
obtained from the same sample at only slightly different
reaction times, or under varying conditions. Stone and Waters
recognized that under the usual conditions of base in aqueous
alcohol, o-quinones usually gave complex asymmetric spectra
due to secondary radicals (14). They found that this
difficulty was overcome by using dimethylformamide (DMF) as
the solvent, or by using a flow system, and they were able
to obtain satisfactory spectra for several substituted
o-benzoquinones. They also allowed these quinones to oxidize
further to the secondary radicals which they identified as
due to hydroxylated quinones, and whose spectra they recorded
in both aqueous and DMF solutions. It is noteworthy that this
further reaction is blocked in the case of phenanthrenequinone,
one of the few o-quinones for which a well resolved spectrum
had been available.

This situation is reflected in the natural abundance of
various naphthoquinones. In a book entitled Naturally Occurring
Quinones (15), Thomson writes that only two o- or β-naphtho-
quinones are found in nature. These are both plant products,
diosquinone and dunnione, which has an oxygen atom at C-4 tied
up in a furan ring and readily rearranges to a p-quinone.

However, p- or α-naphthoquinones are quite common, and many
of these are 2-hydroxyderivatives that result from the oxidation
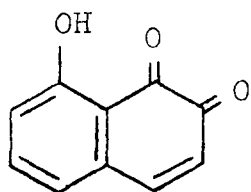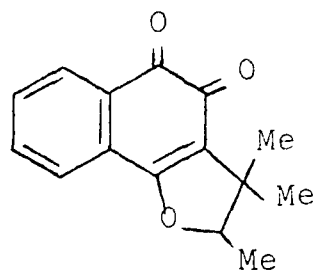
<u>diosquinone</u>   <u>dunnione</u>

of the o-naphthoquinones. Since isolation often involves
alkaline extractions, it is possible that more of these exist
naturally as the o-quinones. The occurrence and chemistry of
many of these compounds are discussed at length in the second
chapter of Thomson's book and in Elsevier (16). Vitamin K_1,
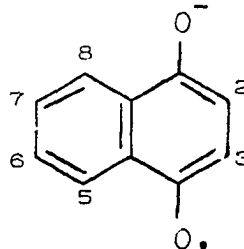for example, has the formula
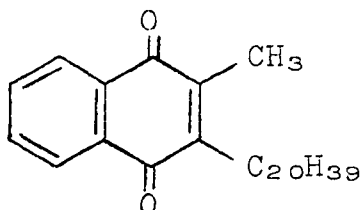
It has been suggested that free radicals observed in electron
transport particles may be naphthosemiquinones related to
vitamin K. The reaction of vitamin K_1 in alkali to give a
transient purple color is known as the Dam-Karrer test and
has been shown by Fieser to give phthiocol as the end
product, and he suggests an o-naphthoquinone intermediate
which readily tautomerizes (17).
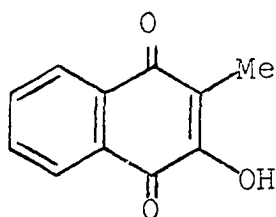
phthiocol

Much recent and past interest in the hydroxyquinone or lawsone compounds has developed as a result of their biological activity. Compounds with certain alkyl substituents at the 3-position show effectiveness as anti-malarials and as coccidiostats and are being examined as potential cancer chemotherapeutics. Variations of the alkyl substituents have included the introduction of cyclohexyl and adamantyl groups, and the syntheses of a large number of such compounds have been reported by Fieser and many of his coworkers over the past twenty years (18).

Unsubstituted 1,4-naphthoquinone gives rise to a radical anion with an esr spectrum due to three pairs of equivalent protons, for which the splitting constants vary slightly with solvent. The following assignments have been made of these constants on the basis of molecular orbital calculations for the benzene ring, and on the basis of changes with substitution for the quinone ring (19, 20):

|	Aprotic Solvents	Aqueous Solvents
$a^H_{2,3}$	3.30 gauss	3.20 gauss
$a^H_{6,7}$	0.64 gauss	0.65 gauss
$a^H_{5,8}$	0.32 gauss	0.50 gauss

Reported spectra from the less symmetrical 2-hydroxy-1,4-naphtho-quinone are somewhat more complicated. The splitting constants given for the radical obtained by reduction with dithionite in aqueous potassium hydroxide, followed by partial reoxidation with air are 1.87 gauss, 1.48 gauss, 0.10 gauss for two hydrogens, and 0.28 gauss. Only the last was assigned and this was attributed to the 3-position, since the 3-methyl substituted compound showed a quartet splitting of 0.35 gauss in place of the 0.28 gauss doublet (21). In another esr study of several substituted 1,4-naphthoquinones, including some lawsone type compounds, Piette and Scheuer and coworkers concluded that an ionized 2-hydroxy group could markedly alter the relative spin density concentration in the quinone and aromatic rings (22). This is illustrated by the contrast in the spectra of lawsone and 2-methoxy-1,4-naphthoquinone. In the latter the largest splitting, 1.65 gauss, is assigned to the 3-position and the methoxy hydrogens are assigned a splitting of 0.75 gauss. The sum of the four benzene ring

splitting constants is less than 2.5 gauss, showing that most
of the spin density has remained in the quinone ring as it
does in 1,4-naphthoquinone itself. In the present study an
attempt is made to clarify the assignments of the different
spectra obtained from lawsone in alcoholic or aqueous base,
and in an aprotic solvent such as dimethyl sulfoxide.

The lawsone radical anion shows little tendency to
oxidize further. However, other products from the oxidation
of o-naphthoquinone have been reported. The so-called
Wichelhaus oxide was first synthesized in 1897 (23) and the
reaction leading to its formation was studied by Hooker and
reported in one of a series of posthumous papers on related
systems written from Hooker's notebooks by Fieser and
published in 1936 (24). Samples obtained from this work have
served as a basis for Fieser's current studies on the chemo-
therapeutic effects of these systems. Very recently Fieser
added to this work by using nmr to determine the correct
structure of this oxide, obtained by ferric chloride oxidation
of o-naphthoquinone (25). Thomson has reported that oxidation
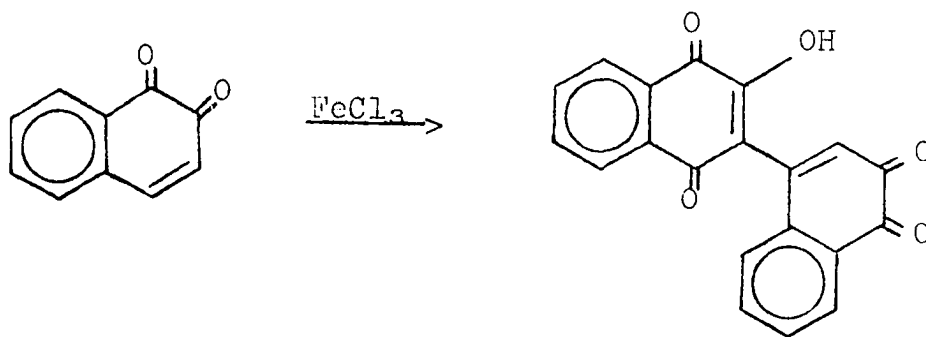
of 1,2-dihydroxynaphthalene gives a quinhydrone that is

converted to lawsone by excess oxygen (5). He also mentions
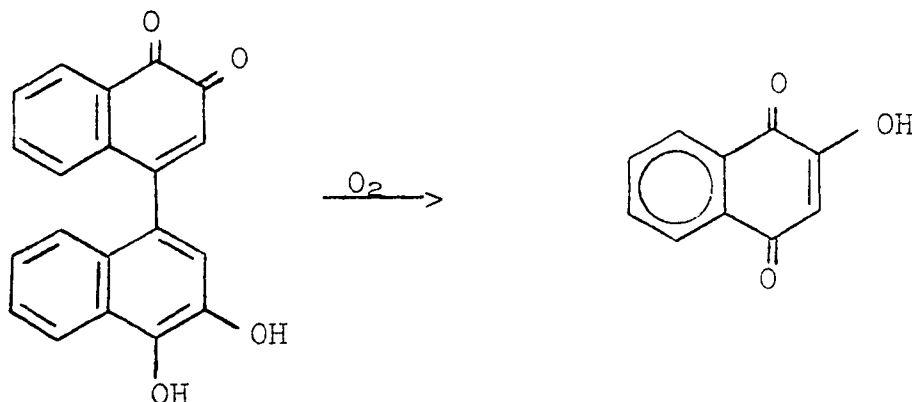
that the base-catalyzed autoxidation of β-tetralones results

in a blue color, which rapidly changes to the red of the

lawsone anion. This blue color is used as a test for β-

tetralones, and is postulated to be due to an anion formed

by Michael addition of the enolate anion of β-tetralone to

its initial oxidation product, o-naphthoquinone (26). Excess
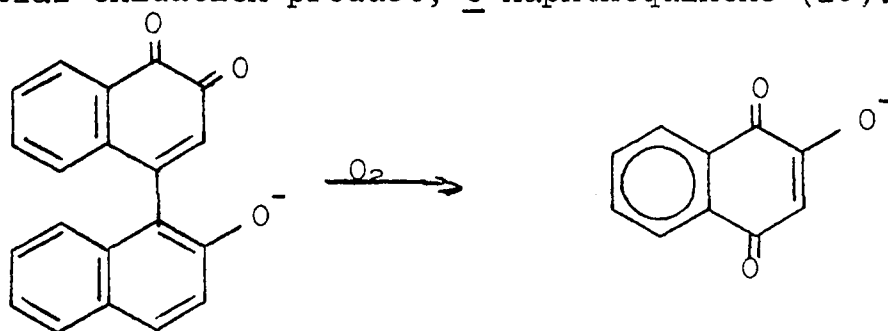
oxygen then converts this species to lawsone, as in the case

of the quinhydrone. As will be seen in the present study,

the stability of the lawsone anion system is further

emphasized in its formation from the oxidation of such widely

different compounds as 3-benzosuberone (I) and barbaralone (II)
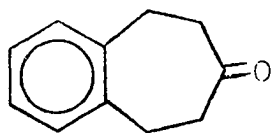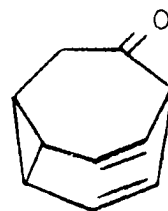
I   II

In some previous work in this laboratory, an esr signal
was obtained on mixing cycloheptatriene and an excess of
potassium t-butoxide in dimethyl sulfoxide (DMSO) (27). The
spectrum was not that of the known cycloheptatriene radical
or radical ions. Further attempts have now been made to
identify this species through the closer examination of the
reaction system itself and the esr behavior of many seven- and
eight-membered ring compounds which might possibly be formed
from that system. The results of these studies will be
presented in the latter part of this thesis.

RESULTS AND DISCUSSION

Tetralones and o-Naphthoquinones

If one adds oxygen to a sample of α-tetralone in
potassium t-butoxide and dimethyl sulfoxide, one might
expect to observe the formation of a semidione analogous
to that formed from cyclohexanone under the same conditions.
β-Tetralone could undergo the same reaction, giving two
different semidiones, one of them identical to the α-
tetralone product. When the α-tetralone system was examined,
it was indeed found to produce paramagnetic species. How-
ever, the initial esr spectrum which was seen immediately
after oxygen was added disappeared within a few minutes,
and a new signal appeared which was stable indefinitely.
At this point the solution had become deep red in color.
If more oxygen was added to the sample, the initial radical
(Radical A) reappeared and eventually changed to the second
species (Radical B). β-Tetralone gave a different initial
radical which was rapidly replaced by Radical A which again
went on to Radical B. The hyperfine splitting constants
for A and B are as follows:

Radical A $a_H = 3.95, 1.45, 1.05, 0.4, 0.2$

Radical B $a_H = 2.5, 1.5, 0.5, 0.1$

All are doublet splittings. The initial radical from β-tetralone appears to be due to two hydrogens with hfsc about 1.4 gauss. It is a broad triplet and too short-lived for further resolution. No changes in any of these spectra were observed in d_6-DMSO, which usually results in exchange of α-protons in semidiones. These results did not seem consistent with simple semidione formation.

Thomson had reported that oxidation of both α- and β-tetralone in potassium t-butoxide in t-butyl alcohol gave 50-70% yields of 2-hydroxy-1,4-naphthoquinone, or lawsone (5). The reaction scheme proposed involved the intermediacy
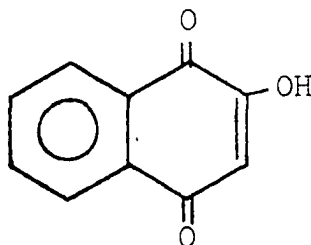

lawsone

of o-naphthoquinone, a suggestion supported by its conversion to lawsone under similar conditions. The first intermediate quite probably is the α-diketone which enolizes rapidly in the strong base to the hydroquinone dianion which then gives the semiquinone radical anion by electron transfer. It appears that this is the sequence observed in the esr experiment with the tetralones and that reaction is so rapid that the diketone radical anion is never seen.

15
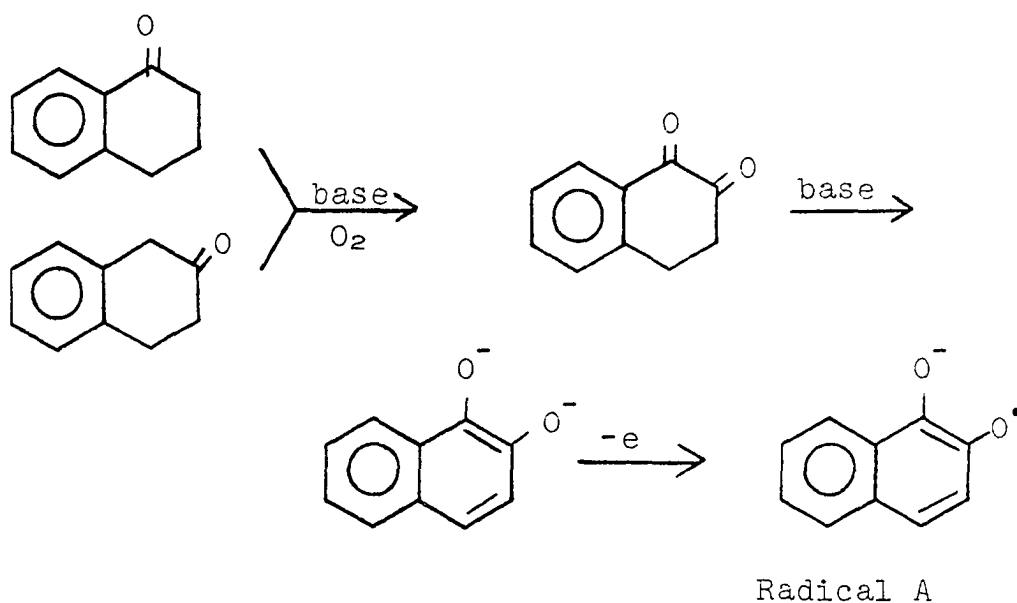
Radical A

o-Naphthoquinone itself in potassium t-butoxide-DMSO
gave an initial spectrum identical with Radical A which
changed with time to that of Radical B, which in turn was
the initial radical seen from lawsone. The lawsone radical
anion solution was deep red and the signal from it did not
change over a period of twenty-four hours. This oxidation
can proceed as follows:
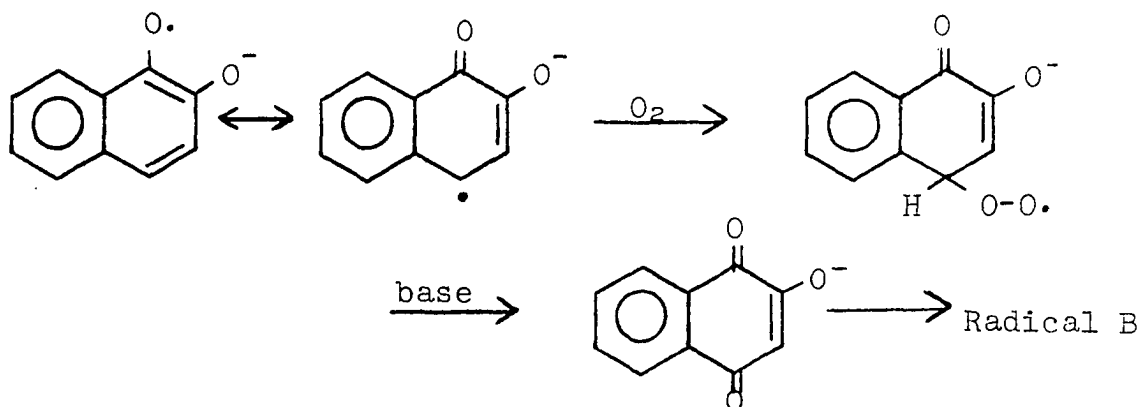
The oxidation product of o-naphthoquinone with ferric chloride, or of α-tetralone with selenium dioxide, is the so-called Wichelhaus oxide, mentioned in the introduction (23). It was prepared and its esr behavior examined under the same conditions as the tetralones and naphthoquinones. A poorly resolved esr signal was seen, but it was different from any of those previously seen, so that this oxide was eliminated as a possible source of Radical A or B. It thus was concluded that Radical A is the o-naphthosemiquinone and that Radical B is a radical anion of the 2-hydroxy-1,4-naphthoquinone lawsone. Radical A could also be generated from o-naphthoquinone using propiophenone anion in DMSO or dimethyl formamide (DMF) as an electron transfer agent, or by using zinc and potassium hydroxide in DMF as the reducing system. The same conditions produced Radical B with lawsone.

These radicals have been observed from much less likely precursors than the tetralones. 3-Benzosuberone or 4,5-benzocycloheptanone, was examined, again with the expectation that a cyclic unsaturated semidione might be formed. In the potassium t-butoxide-DMSO system with added oxygen, an esr signal was observed which again proved to be Radical A and within minutes was replaced by the spectrum of Radical B. Here it can also be postulated that a diketone is initially formed, but that it is now oxidized further at a highly activated benzylic position to the triketone.

Previous work in this laboratory has shown that triketones rapidly decarbonylate to diketones (27), which in this case would give the same intermediate diketone that was invoked for the tetralones, and the same reaction sequence giving A and B could follow.
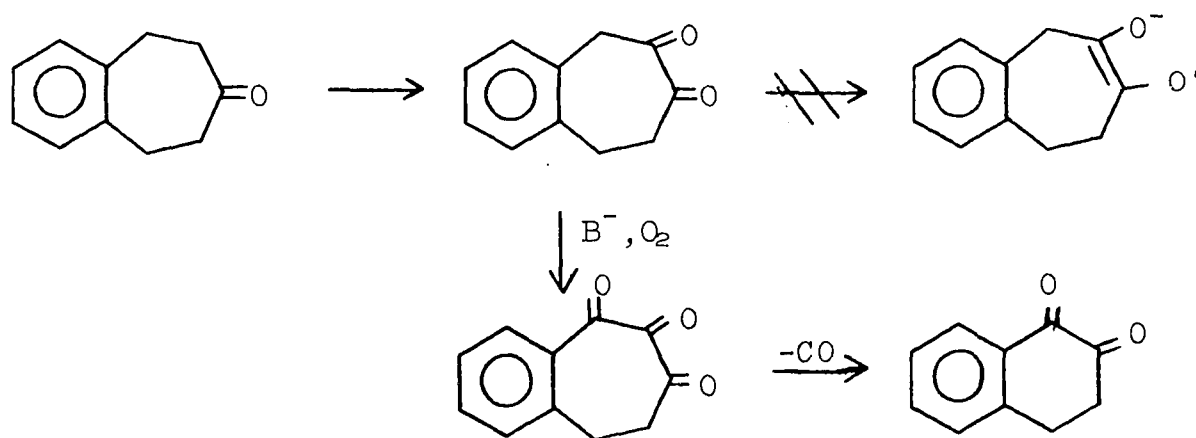
A more unusual system which gives the lawsone radical anion as a product is another ten carbon atom compound,
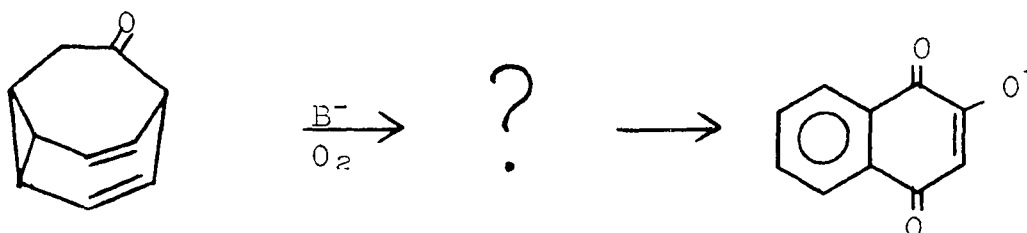
the ketone barbaralone.[a]   There is some precedent for the

skeletal rearrangement involved in the isomerization of

bullvalene to dihydronaphthalene, although the conditions

needed to bring about the latter are much more severe.

9,10-Dihydronaphthalene is the first isolable product of

thermolysis of bullvalene at 350° (28), and is also the

final product when photolysis is followed by thermolysis

of the photoproducts (29).
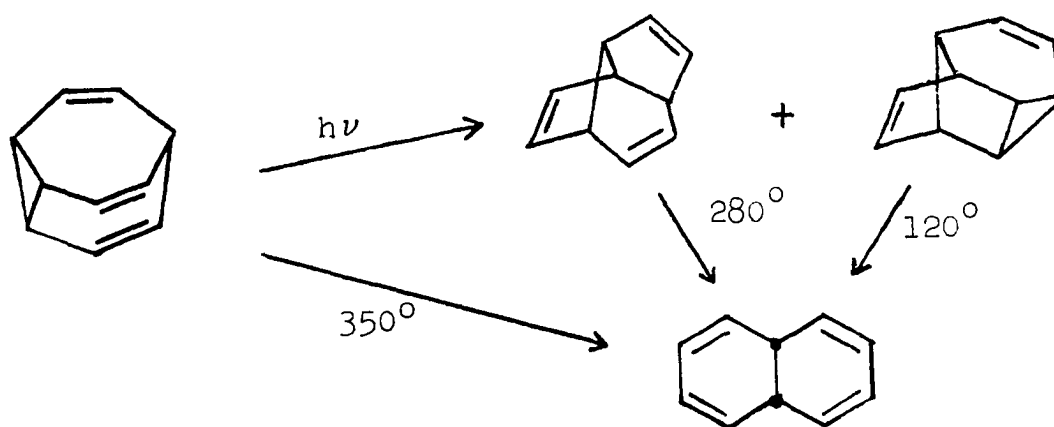
Making use of the reactions above it is now possible

to assign specific splitting constants to the various

hydrogens in Radical **A** and Radical **B**.   The only previous

reference to an esr spectrum from o-naphthoquinone was by

---

[a]Dr. R. S. Givens, Ames, Iowa.   Preparation and esr
spectrum of barbaralone.   Private communication.   1967.

Adams, Blois and Sands who reported a 17 line spectrum,
from reduction of the quinone in aqueous base, with spacings
of 1.3 ± 0.2 gauss and 0.24 ± 0.04 gauss (8). No further
analysis or assignment was made. The lack of more clearly
defined spectra has probably been due to the complication of
the further oxidation to the hydroxyquinone. The only
reported spectrum from lawsone was also taken in aqueous
base (21) and could be closely reproduced in aqueous t-
butyl alcohol from the lawsone that gave Radical B in
potassium t-butoxide-DMSO.

The availability of methoxy and methyl substituted
tetralones suggested their use in generating substituted
naphthoquinones. Since spin density must be transmitted
through an oxygen atom to the methyl hydrogens of a methoxy
group, splitting by these hydrogens is much lower than that
by hydrogens attached directly to the ring. Therefore a
great reduction in or loss of a splitting constant when a
methoxy substitution is made implies that splitting was due
to the hydrogen at the position of substitution. A methyl
substituent, on the other hand, causes little change in
the magnitude of the splitting constant but the doublet
which is seen from one hydrogen becomes a quartet due to
the three equivalent methyl hydrogens. The loss of the
largest splitting in the o-naphthoquinone radical anion
when it was further oxidized at the 4-position implied

that this splitting was due to the 4-hydrogen. This was confirmed by the spectrum from 4-methyl-1-tetralone which showed a quartet splitting of 4 gauss. Splitting constants for the various o-naphthosemiquinone ions are given in Table 1.

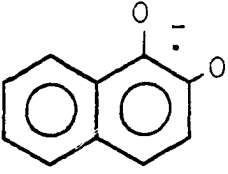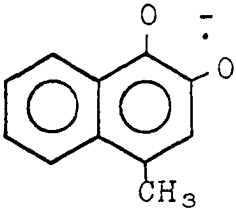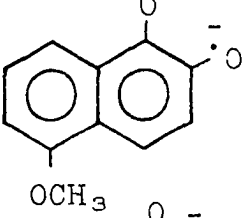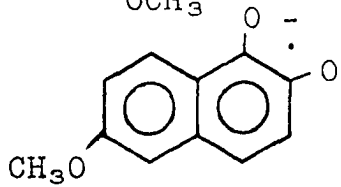Table 1. Hfsc for o-naphthosemiquinone radical anions
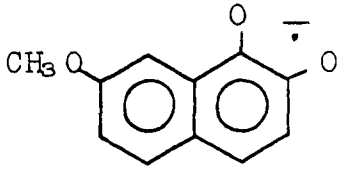
| Starting compound	Radical anion	Hfsc
1-Tetralone		3.95 1.45 1.05 0.40 0.20
4-Methyl-1-tetralone		4.00 (3H) 1.40 1.05 0.34 0.20
5-Methoxy-1-tetralone		4.00 1.45 0.98 0.50 0.18
6-Methoxy-1-tetralone		4.20 1.08 0.40 0.26 0.13 (3H)

Table 1 (Continued)

Starting compound	Radical anion	Hfsc
7-Methoxy-1-tetralone		3.90 1.40 1.20 0.10

The very small change on substitution at the 5-position
indicates a very low spin density at this position, since the
hfsc must be less than 0.10 gauss. The appearance in the
6-methoxy compound of a 0.13 gauss quartet, and loss of the
1.4 gauss doublet which is present in every other case
compels the assignment of this 1.4 gauss splitting to the
6-position. In the case of 7-methoxy substitution, it is
the splitting of approximately 0.4 gauss which is lost,
and the methoxy splitting, by analogy with the 6-methoxy
case, would be anticipated to be less than 0.04 gauss, too
small to be resolved. Of the remaining two constants of
about 0.2 and 1.0 gauss, the larger is assigned to the
8-position and the smaller to the 3-position. From simple
resonance pictures it is clear that high spin density at
position 4 comes at the expense of position 3. In the
benzene ring, position 8 is conjugated with position 6 which
has already been assigned a relatively high splitting constant.

These are the positions which are ortho and para to the
semiquinone functional group, positions which show the
largest splittings in phenyl methyl semidione (30),
phenanthrenesemiquinone (11) and the isatin radical anions
(31). The complete assignments for the o-naphthosemiquinone
anion, Radical A, are thus as follows:

1.05

0.40

O $\overset{-}{\cdot}$

O

1.45

0.20

<0.10   3.95
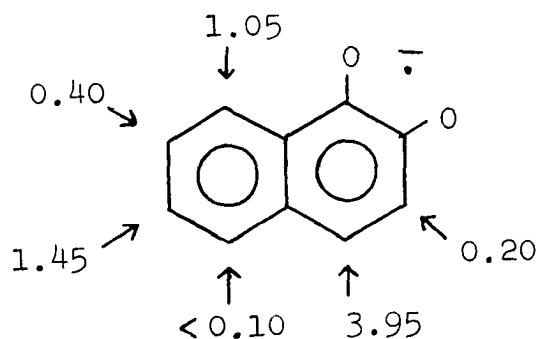
The similarity of the benzene ring splittings to those
assigned for phenanthrenesemiquinone by molecular orbital
calculations can readily be seen. Similarly in the isatin

$\overset{-}{O}$ $\overset{\cdot}{O}$

1.35

0.20

0.40   1.67
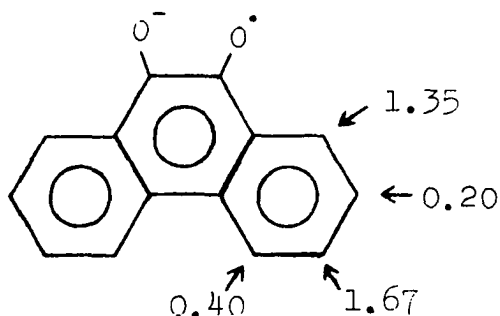
radical anion (III) the o- and p-splittings, which have not
been differentiated, are 3.73 and 3.17 gauss while the
meta hydrogen splitting is only about 1 gauss. The sulfon-
amide radical anion IV is another heterocyclic compound

with a similar functional group. Its esr spectrum also shows two larger splittings of 2.70 and 3.75 gauss and two smaller ones of 0.75 and 0.95 gauss for the ring hydrogens.[a]
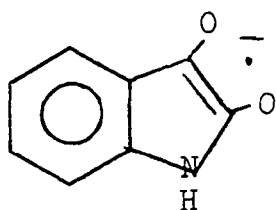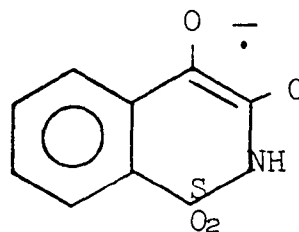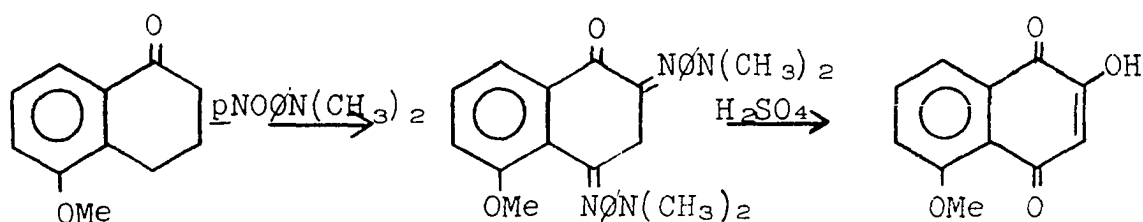

III   IV

The initial transient signal from β-tetralone has still not been explained. It is a broad triplet, with spacing of approximately 1.4 gauss, and is too short-lived for further resolution. The previously mentioned anion postulated as the cause of the blue color which initially develops when β-tetralone is mixed with base is a possible source of this spectrum (26). Since coupling occurs at the 4-position, the 4.0 gauss splitting would not be seen. The broad triplet may then in fact be two nearly overlapping doublets with hfsc of approximately 1.4 and 1.1 gauss, which are the larger splittings in the benzene ring of the o-naphthoquinone, with the smaller splittings unresolved.

---

[a]R. Blankespoor, Ames, Iowa. Esr spectra of some heterocyclic semidiones. Private communication. 1969.

After periods of time in the esr cell varying from
fifteen minutes to several hours, the naphthoquinone spectra
from the substituted tetralones are replaced by the spectra
of secondary radical species, presumably substituted trioxy-
naphthalene radical anions of the lawsone type. The identity
of the spectra from the air oxidation of 5-methoxytetralone
in base and DMSO and from independently synthesized 5-
methoxylawsone with propiophenone anion is additional
evidence that this is the reaction involved. The following
known reaction sequence was used for this synthesis:

$$\text{(5-methoxytetralone)} \xrightarrow{\underline{p}NO\emptyset N(CH_3)_2} \text{(bis-dimethylaminomethylene tetralone)} \xrightarrow{H_2SO_4} \text{(5-methoxylawsone)}$$

From the effects of substituents on the splitting patterns
it is again possible to assign the various hfsc in the
parent system. For the quinone ring, information was
obtained from the commercially available 3-methyl derivative
known as phthiocol. Splitting constants for the various
substituted lawsone spectra obtained in potassium t-butoxide-
DMSO are given in Table 2.

Table 2. Hfsc for substituted lawsone radical anions in

potassium t-butoxide-DMSO

| Starting compound	Structure	Hfsc of radical anion (in gauss)
Lawsone		2.50 1.50 0.50 0.10
Phthiocol		2.50 1.45 0.55 0.40 (3H) 0.08
5-Methoxylawsone		2.50 1.40 0.30
6-Methoxylawsone		1.30 0.45 0.30 0.15 (3H)
7-Methoxylawsone		2.30 1.85 0.60

In phthiocol the 0.4 gauss quartet is clearly due to

the 3-methyl group. Since this splitting is seen in

addition to all of the splittings in lawsone itself, it

appears that a hydrogen in the 3-position is not seen in

the parent compound. Some results with 4,5-benzocyclo-

heptanone reinforce the belief that the 3-hydrogen is not seen. If this ketone is allowed to exchange in base and deuteromethanol, greater than ninety-five percent deuteration of the four alpha positions can be obtained. This deuterated species gives the same lawsone spectrum as the undeuterated material. In any reasonable mechanism for converting the seven membered ring to the quinone and the hydroxyquinone, one of the deuterium atoms is retained at the 3-position. Since no splitting is lost when the 3-position is deuterated, no splitting in the original spectrum can be attributed to the 3-hydrogen.
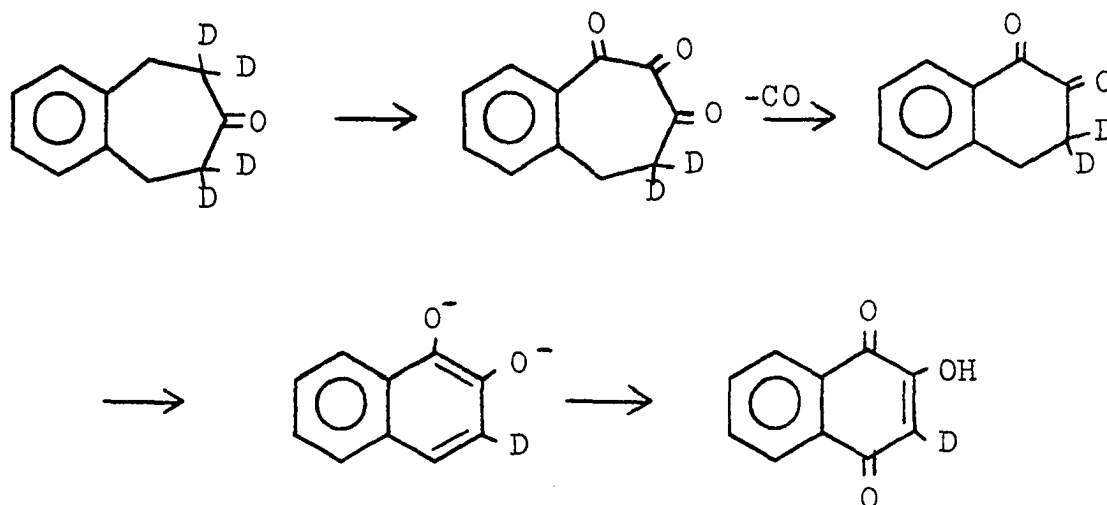
All four splittings in the lawsone radical anion are thus due to the benzene ring. A splitting constant of about 1.5 gauss is present in the 5-, 6- and 7-substituted compounds, so this may immediately be assigned to the

8-position. The 2.5 gauss splitting is present in the
5- and 7-compounds, but has been replaced in the 6-compound
by a small, 0.15 gauss quartet, which is reasonable for
splitting by a methoxy group. Of the two remaining small
splitting constants, although their size is somewhat
different than in the parent compound, the larger is present
for the 6- and 7-substituted compounds and the smaller for
the 5- and 6- but not the 7-compound. This suggests that
the smallest splitting in the parent compound be assigned
to the 7-position. The complete assignments for the lawsone
radical anion in DMSO are then as follows:
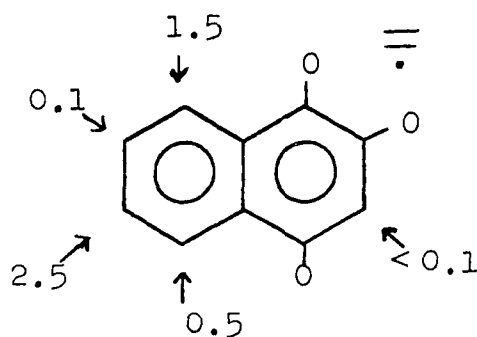
These values change slightly with solvent. Exact
splitting constants for two different solvent systems are
shown in Table 3.

A very different spectrum is obtained in aqueous media.
The best resolution of this radical was seen in 80% aqueous
t-butyl alcohol with propiophenone anion as the reductant.

Table 3.   Exact hfsc for lawsone radical anion in different
          solvents

Solvent	a_5^H	a_6^H	a_7^H	a_8^H
DMSO	0.56	2.52	0.10	1.52
50% t-butyl-alcohol-50% DMSO	0.48	2.35	0.13	1.48

This signal is quite similar to that which Hollocher reported for lawsone in dilute aqueous potassium hydroxide with radium dithionite (21). From the data for these radicals given in Table 4 it appears that a splitting of 0.25-0.30 gauss is due to a hydrogen at position 3, since methyl substitution replaces a doublet with a quartet of about the same magnitude rather than giving an additional splitting as was seen in the spectrum in DMSO. It is not known whether any smaller splittings in the methoxy compound were not present, or not resolved.

The splitting patterns of the lawsone radical ions are much more similar to those of ortho than of para semiquinones. This is somewhat surprising since para quinones are usually considered to be much more stable. However, the esr spectra of the two systems are quite

Table 4. Hfsc for lawsone radical anions in aqueous solvents

Compound	Solvent-base system	Reducing agent	Hfsc
Lawsone	80% t-butyl alcohol-KOH	propiophenone anion	1.90 1.50 0.25 0.15±.02 0.10±.02
Lawsone[a]	0.1 N aqueous KOH	sodium-dithionite	1.87 1.48 0.28 0.10(2H)
Phthiocol[a]	0.1 N aqueous KOH	sodium-dithionite	1.23 0.98 0.35(3H) 0.08(2H)
3-Methoxy-lawsone[b]	0.1 N aqueous NaOH		1.80 1.50 0.20

[a]Source (21).

[b]Dr. Franz A. Neugebauer, Heidelberg, Germany. Esr spectra from reduction of quinones. Private communication. 1968.

distinct, and the spectra of the lawsone ions indicate

that they are most accurately represented by ortho

naphthosemiquinone structures having oxygen substituents

at the 4-position.

A possible explanation for the fact that the 3-hydrogen

is seen in one solvent system but not the other is that

different ionic species are being observed in the different

solvent-base systems. If the substituent on the o-semi-

quinone at the 4-position is a hydroxyl group, it can be

further ionized in strong base to give a dianion radical

which would be expected to exchange extremely rapidly

with the solvent. If the semiquinone function is localized

at the 1,2-positions, the 3,4-positions may be viewed as a

keto-enol system, and hydrogens at the 3-position will be

involved in the exchange. In deuterated solvents compounds
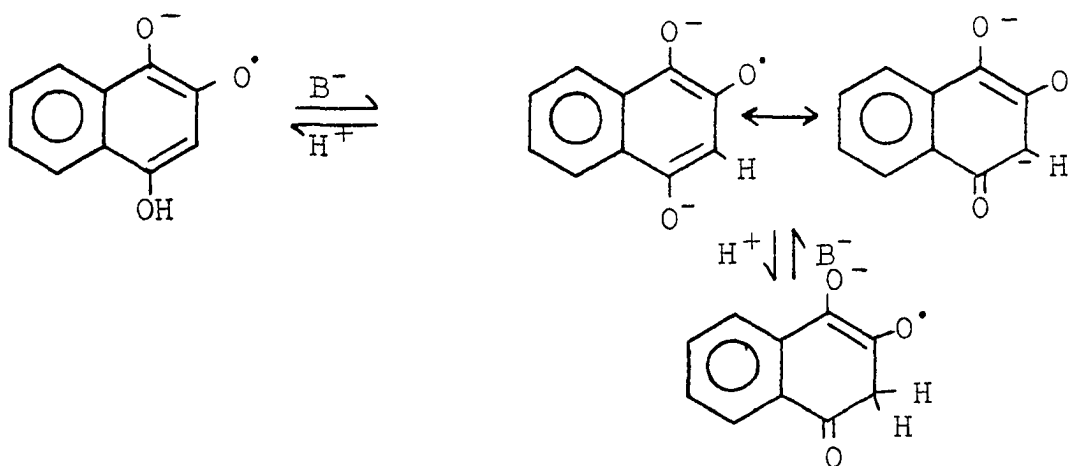
of this type have been shown to incorporate deuterium at
the 3-position (22). It is suggested that in the strongly
basic potassium t-butoxide/DMSO, the rate of this exchange
is so rapid that the 3-hydrogen is never seen by esr. A
methyl group at this position, however, cannot be ionized,
and is responsible for a splitting of 0.4 gauss, a value
similar to that attributed to the 3-hydrogen in the radical
in aqueous or alcoholic potassium hydroxide where the rate
of exchange is slowed sufficiently that the hydrogen can be
seen by esr.

Because the spectra in the different solvents appear
to be due to two different radicals, it may be that in
the more strongly basic aprotic potassium t-butoxide-DMSO
the equilibrium is such that the dianion radical is the
predominant species observed in the esr, whereas in aqueous
solutions protonation occurs to a much greater extent
making the monoanion radical the prevalent one. If this
is the case the dianion radical may be represented as an
o-naphthosemiquinone with an $-O^-$ substituent at the 4-
position. This substituent is a strong electron donor, and
increases the spin density in the benzene moiety, which is
reflected in its having larger splitting constants for the
ring hydrogens than the parent semiquinone has. In the
monoanion radical, the -OH substituent is not so strong
an electron donor and the spin density in the benzene ring,

as indicated by the hfsc, is intermediate between the other
two cases. This type of argument has previously been
invoked to explain substituent effects on esr spectra of
substituted naphthazarins (22).

Additional hydroxyl substitution in the benzene ring
causes drastic changes in the esr signals of lawsone type
compounds in potassium t-butoxide-DMSO. Both synthetic
and commerical juglone, or 2,5-dihydroxy-1,4-naphthoquinone,
gave a complex, apparently unsymmetrical spectrum of
approximately 58 lines. Since hydroxyl splitting is not
usually seen in these compounds, the maximum number of
lines expected would be 16, from four non-equivalent
hydrogens. Possibly some type of condensation is occurring
in the strong base. Fiette and Scheuer have reported a
spectrum of electrolytically reduced juglone in a deuterated
solvent which has presumably deuterated the 3-position.
Analysis gave the following hfsc (22):
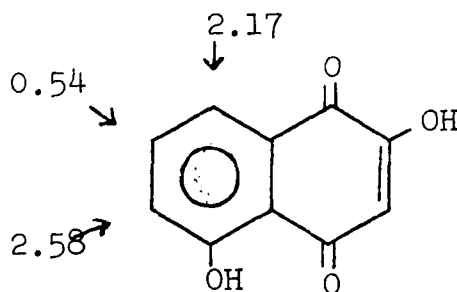
Juglone

These are in the same order as the previously discussed
o-naphthoquinones. The somewhat higher values may again
be ascribed to the additional electron donating effect of
a second hydroxyl group.

Another type of substitution also results in some
changes in spin density. When the heterocyclic compound
below was oxidized in potassium t-butoxide-DMSO, a signal
was obtained which gave the listed splitting constants.[a]
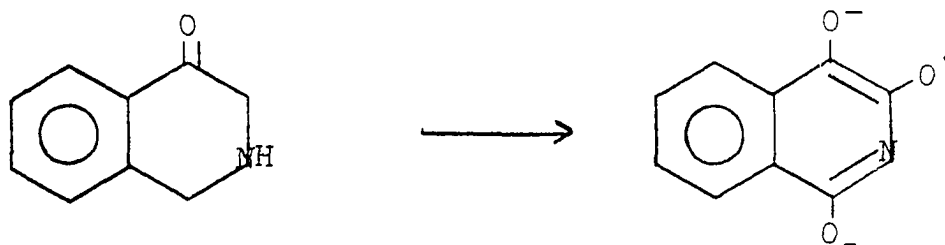
a^H = 2.82, 1.91, 0.775 and 0.350 gauss

Although precise assignments have not been made, we still
see the typical pattern of two larger and two smaller
splittings due to the benzene ring hydrogens.

Splitting patterns and spin densities for the highly
symmetrical p-quinones have been predicted and explained
with considerable success by various molecular orbital
calculations (11, 12). These calculations seemed to be

[a]R. Blankespoor, Ames, Iowa. Esr spectra of some
heterocyclic semidiones. Private communication. 1969.

much less satisfactory for most o-quinones, perhaps due to
the lack of sufficient experimental data as much as to
inadequacies in the calculations. It was decided to
compare the experimentally obtained spin distribution
in o-naphthosemiquinone with that predicted by simple
Huckel molecular orbital (HMO) calculations. The data in
Table 6 show the calculated spin densities for several
trials, varying the coulomb integrals (α_o) for the two
oxygen atoms. Values of h_o from the equation

$$\alpha_o = \alpha_c + h_o \beta_{cc}$$

were chosen in the same range as those which have been
used for other quinone calculations. It is obvious that
none of these sets of calculations gives satisfactory
agreement with the experimentally obtained values, or
even with the trends observed at the different ring
positions. For instance, in all cases the spin density
predicted for the 5-position is much too high, considering
the fact that no splitting due to this position is seen
by esr. Poor agreement is obtained where the two oxygen
atoms are treated as being equivalent. In cases where
the values seem appropriate for the quinone ring, those
in the benzene ring are less satisfactory. In the first
three columns, the densities at the 5,8-positions are
larger than those at the 6,7-positions rather than 6,8-

Table 5. Spin Densities Calculated from Simple Huckel MO Program

h_o	$O^{11}=O^{12}=1.5$	$O^{11}=1.5,$ $O^{12}=2.0$	$O^{11}=2.0,$ $O^{12}=1.5$	$O^{11}=1.5,$ $O^{12}=1.0$	$O^{11}=2.0,$ $O^{12}=1.0$	Experimental[a]
ρ_3	.0003	.0013	.0000	.0093	.0090	.0083
ρ_4	.1554	.1803	.1491	.1126	.1024	.1645
ρ_5	.0625	.0770	.0700	.0406	.0425	< .004
ρ_6	.0458	.0432	.0574	.0476	.0574	.0604
ρ_7	.0341	.0422	.0319	.0231	.0196	.0166
ρ_8	.0731	.0780	.0922	.0639	.0774	.0438

[a]Calc. from $a_H = Q\rho$, using $Q = 24$.

larger than 5,7- as is seen experimentally. In the last
column the correct alternation is showing up but 8 is
still greater than 6, and 5 is still much too large.
It may be that a set of parameters would eventually be
chosen which would give more exact agreement with the
data, but such a haphazard system seems to be of little
predictive value.

Simple resonance structures can also be used to depict
pathways of delocalization in radicals. The size of a
given hfsc can be used to assign the relative importance
of a structure with the unpaired electron at that position
in the set of resonance structures. In some cases the
choice is obvious without knowing the esr data. For
example, the two structures below clearly indicate that
splitting at the 4-position should be greater than at
the 3-position.
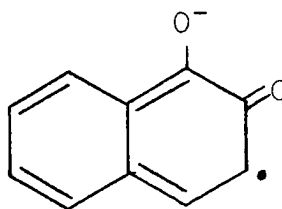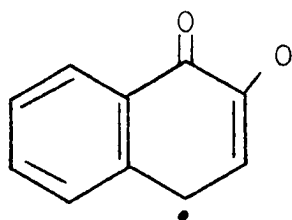
It is less obvious why the following order of importance
should hold:
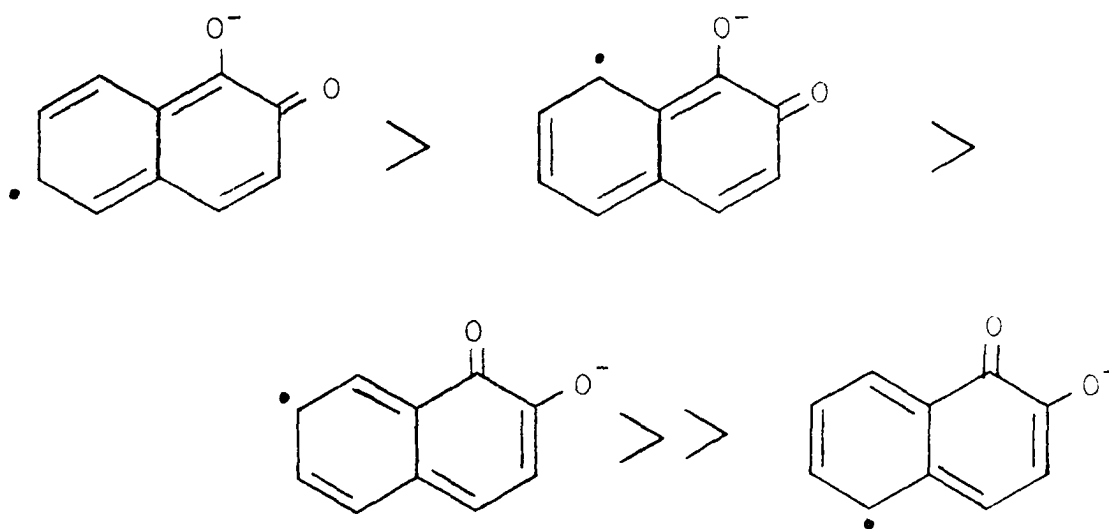
Arguments based on resonance structures again constitute
more of a rationalization than an explanation.

Cyclic Unsaturated Semidiones

Seven and Eight Membered Ring Semidiones

Attempts at the generation of cyclic unsaturated semidiones were largely unsuccessful due to the synthetic problems involved in specifically placing multiple oxygen functions in unsaturated systems. Several of the unsaturated seven and eight membered ring monoketones are known compounds, but the corresponding α-diketones or α-hydroxyketones have not been reported. One exception is the purported yield of 10% of 4-cycloheptene-1,2-dione from the lithium aluminum hydride reduction of α-tropolone (32). The only characterization of this product was from
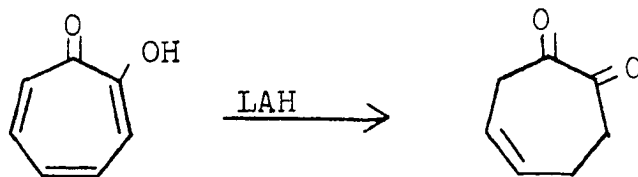
the ultraviolet spectrum of the 2,4-DNP derivative which was said to be consistent with that of a seven membered ring α-diketone with a non-conjugated double bond. This reaction was repeated several times on one gram batches of α-tropolone. In the most successful case about 80 mg of a yellow oil was obtained which darkened rapidly in air and could not be well characterized. In potassium t-butoxide-DMSO, and with added propiophenone, no esr signal could be seen, indicating that little or no

diketone was present. Direct reduction of _α_-tropolone in
the esr cell with sodium-potassium alloy in dimethoxy-
ethane (Na-K in DME) also failed to yield any radical
species.

Oxidative approaches to semidiones from mono-ketones
usually involve direct oxidation in basic solution,
formation of the diketone _via_ selenium dioxide, or
introduction of _α_-bromo- or _α_-acetoxy- substituents with
subsequent conversion to the _α_-hydroxyketone. The direct
oxidation was attempted on all of the following compounds
by addition of air to solutions of the ketones in
potassium _t_-butoxide in DMSO:
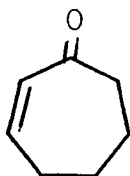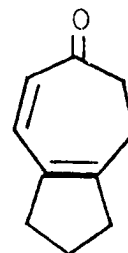
2-cycloheptenone
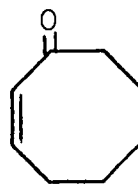
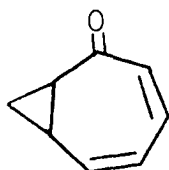2-cyclooctenone
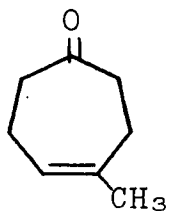
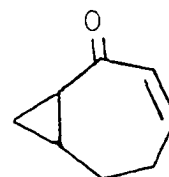4-methyl-4-cycloheptenone
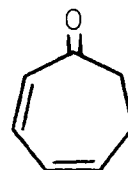
2,4-cycloheptadienone
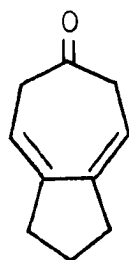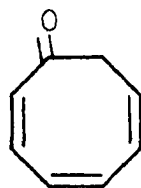
4,5-trimethylene-2,4-
cycloheptadienone

4,5-trimethylene-3,5-
cycloheptadienone

2,3-homotropone

4,5-dihydro-2,3-homotropone

2,4,6-cyclooctatrienone

None of these experiments produced an observable radical. In some of these cases a stable enolate anion apparently forms which is resistant to oxidation. With the cyclooctatrienone, for example, a deep blue green color appears in the basic DMSO solution which persists for several days.

van Tamelen had reported that several attempts to oxidize the 2,4-cycloheptadienone, including oxidation with selenium dioxide, yielded only the dehydrogenation product, tropone (33). An attempt in the present study to oxidize

the 4-methyl-4-cycloheptenone with selenium dioxide
yielded only polymeric materials. α-Bromination is
unlikely to occur where double bonds are present and
acetylation with mercuric acetate occurs primarily at
allylic positions. The unsaturated mono-ketones themselves
are rather unstable, showing a tendency to condense or
polymerize under many reaction conditions. The in situ
acyloin condensation technique which has proved useful
in the synthesis of many bicyclic semidiones from
diesters has thus far been unsuccessful in effecting a
similar reaction with simple unsaturated diesters (34).

There did appear to be one possible sequence for
forming unsaturated α-hydroxyketones. Cohen and Tsuji had
reported the formation of α-hydroxyketones in good yields
when epoxides were allowed to oxidize in air in DMSO with
catalytic amounts of boron trifluoride etherate (35).
Cope, in turn, had published a synthesis of the mono-
epoxide of 1,3-cyclooctadiene (36). His procedure,
involving direct epoxidation with peracetic acid was
repeated in 1,3- and 1,5-cyclooctadiene. In both cases
good yields of the monoepoxides were obtained. When these
were heated in DMSO with added boron trifluoride etherate
with stirring in air for times varying from 10 to 80 hours,
the reaction mixtures turned deep yellow. Samples of these
solutions with added potassium t-butoxide did give strong

esr signals. From the 1,3-diene, the signal was a triplet with splitting of 3.8 gauss, with considerable broadening probably due to unresolved small splittings. From the 1,5-diene a sharp quintet was seen, indicative of four equivalent protons with splitting of about 4.5 gauss.

The species responsible for the esr signals could not be isolated readily from the DMSO solution. Aqueous extraction apparently removed hydroxyketone as well as DMSO. Distillation of the reaction mixtures gave unreacted epoxide and DMSO leaving small amounts of residue which still contained DMSO. However, infrared analysis of the residue from the 1,5-diene epoxide showed both hydroxyl and carbonyl absorptions which had not been present in the starting epoxide. These indications and the esr results are consistent with the following conversions having taken place:
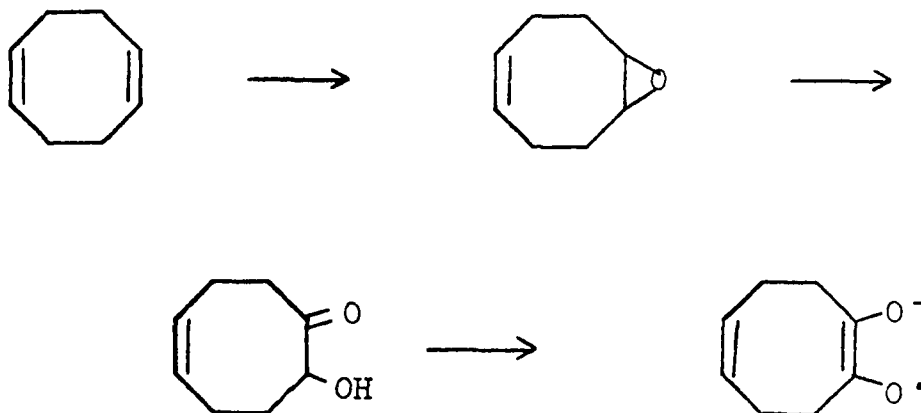
The saturated cyclooctane-1,2-dione gives an esr
signal due to four approximately equivalent α-hydrogens
with hfsc of 3.3 gauss (1). It seems reasonable that the
triplet and quintet from the present compounds also be
attributed to their α-hydrogens. Since the spectra could
indicate a rapid interconversion of different conformations
leading to apparent equivalence of the α-hydrogens it
was decided to look at the spectrum from the 1,5-compound
at lower temperatures, in hopes of freezing out this
interconversion and observing the different conformers.
However, a sufficient radical concentration could not be
maintained at low enough temperatures to observe any change.
As long as a signal could be seen, to about -30°, it was
still the quintet due to four equivalent hydrogens.

When this reaction series was attempted in 1,3-cyclo-
heptadiene, no radical was obtained from the epoxide-DMSO
mixture. The epoxide was formed in much lower yield, and
may be less stable. The 1,4-diene may be a more promising
candidate for hydroxyketone formation since the unconjugated
1,5-diene reacted more readily in the eight membered ring
compounds. There is also a trial and error aspect to the
sequence in that the reaction times of the oxidation vary
so widely. Several attempts to form a mono-epoxide from
cycloheptatriene yielded only starting material and polymer.

Cope had also reported formation of the monoepoxide of

cyclooctatetraene (37). A previous attempt at oxidizing
it in DMSO was said to yield no hydroxyketone (38). This
was repeated with the idea that esr might be able to detect
the presence of very small amounts of the cyclooctatetraene
semiquinone, even though the hydroxyketone could not be
isolated. After the epoxide was heated and stirred in
DMSO, as above, a sample of the mixture did give a strong
esr signal. However, the splitting pattern appeared to
be due to groups of four and six equivalent protons with
splittings of 0.35 and 1.0 gauss, a pattern inconsistent
with the expected radical which has only six hydrogens.
This may be due to some side reaction product of the
epoxidation or DMSO oxidation. It is interesting to note
that thus far it has not been possible to synthesize the
corresponding diketone, cyclooctatetraenequinone, though
attempts have been reported (39).

The dibenzo-[a,e]-cyclooctatetraene-5,6-dione, however,
has been made,[a] and this compound in potassium t-butoxide-
DMSO with propiophenone gave an esr signal which could be

---

[a]Dr. J. F. Neumer, Wilmington, Delaware, Synthesis of
dibenzo-[a,e]-cyclooctatetraene-5,6-dione. Private
communication. 1968.

closely simulated using the listed hfsc. It is difficult
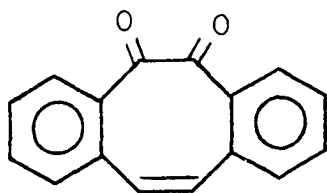
a^H = 0.95 gauss (2H)
0.57 gauss (6H)
0.38 gauss (2H)

to make specific assignments of these splitting constants.
From the structure one would expect five pairs of hydrogens.
Apparently three of these pairs are fortuitously
equivalent. The total width of the spectrum is approximately
the same as that for o-naphthoquinone and phenanthrene-
quinone indicating a similar degree of delocalization from
the semiquinone function through a planar conjugated system.
Neumer, who synthesized the compound, reports that some
other evidence favors a non-planar structure for the diketone.

Some of the difficulties of oxidizing unsaturated
ketones are alleviated if benzo-derivatives are used. The
reactive benzylic position is still a complicating feature,
but the aromatic ring is more inert than the double bond.
It has already been mentioned that the 3-benzosuberone, or
4,5-benzocycloheptenone, did not give a simple semidione,
but a naphthoquinone on oxidation. The 1-benzosuberone,
however, does appear to form a stable semidione when air
is added to a solution in potassium t-butoxide-DMSO. Loss

of the major splittings when the oxidation is done on a
sample in d6-DMSO indicates that these are due to the
α-hydrogens in the semidione. Semiquinones do not exchange
under these conditions. The original attempts to observe
these radicals gave poorly resolved spectra. Recently
Thomas Ku has obtained a highly resolved spectrum with
material from the hydrogenation of benzocycloheptadienone.[a]
The largest splitting, a 6.9 gauss doublet, is quite close
to that of 6.6 gauss which has been assigned to two of the
α-hydrogens in cycloheptanesemidione.[b] In some substituted
benzocycloheptenones which were available, a similar doublet
splitting was seen, and some of the additional fine splitting
was apparently due to aromatic hydrogens. Data from these
compounds indicate that the second largest splitting is due
to the position ortho to the semidione function, as in
previously described semiquinones. The reactions presumably
involved in generating these semidiones are as follows:

---

[a]Thomas Ku. Ames, Iowa. Reduction product of
benzocycloheptadienone and its esr spectrum. Private
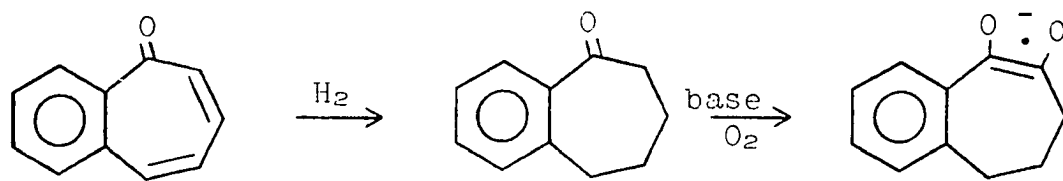communication. 1968.

[b]Robert Keske. Ames, Iowa. Cycloheptanesemidione.
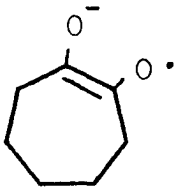Private communication. 1969.
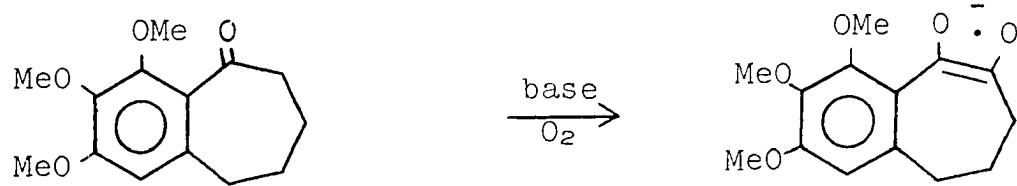
V
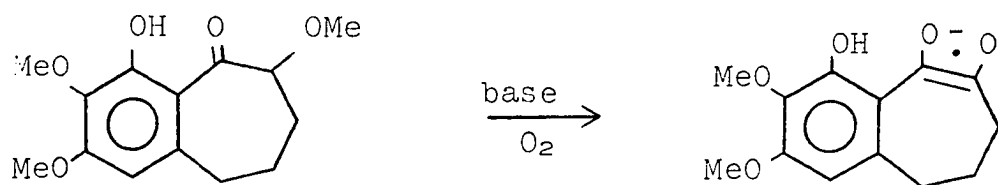
VI

VII

Table 6 . Hfsc for radicals from benzocycloheptanone
derivatives

Radical	Hfsc
V	6.3 0.7 (3H)
VI	6.3 no quartet; other splittings less than 0.5 gauss
VII	6.9 2.5 0.75 (2H) 0.30 (2H) 0.15
(structure: seven-membered ring with O⁻ and O· substituents)	6.6 (2H) 2.05 (2H) 0.28 (4H) 0.56

Ku's analysis for VII shows splitting by seven hydrogens,
which implies delocalization in both aromatic and
aliphatic rings.

It may be possible through substitution to assign
all of these and to compare this system with that of
the cycloheptanesemidione in which all nine hydrogens
have now been assigned by Keske. His experiments show
that one pair of α-hydrogens has hfsc of 6.6 gauss, while
the other pair shows only 0.28 gauss splitting. Since
splitting constants of α hydrogens reflect the dihedral
angle between the semidione function and the α-C-H bond,
one pair of the α-hydrogens must be very close to the
nodal plane: In the benzo derivatives only one large
hydrogen is seen, with the other being less than 0.5
gauss. This indicates a similar conformation for the
benzocycloheptanesemidione and cycloheptanesemidione
itself.

Mystery Radical from Cycloheptatriene

It has been reported in a previous thesis by S. A.
Weiner that an unusual esr signal is obtained from a
mixture of cycloheptatriene and excess potassium $\underline{t}$-butoxide
in DMSO in the absence of air (27). Analysis of the
spectrum indicates splitting due to six hydrogens with
hfsc of 8.2, 7.8, 5.2, and 4.6 gauss for one hydrogen

each and 0.3 gauss for two equivalent hydrogens. Bitropyl,
heptafulvene and tropone were eliminated by Weiner as
sources of the "mystery" radical. The spectrum is not
that of the reported cycloheptatriene radical anion (40)
or radical dianion (41). In the present study the
following related or similar compounds gave no esr signal
when subjected to the same conditions: 1,3-cyclohexadiene,
1,3-cycloheptadiene, 1,3- and 1,5-cyclooctadiene,
norbornadiene, tropone, α- and β-tropolone, 2,3-homotropone,
4,5-dihydrohomotropone and cyclooctatrienone. Cycloocta-
tetraene under these conditions of excess potassium $\underline{t}$-
butoxide in DMSO gave a strong nine line signal due to
eight equivalent protons, presumably from formation of
the cyclooctatetraene radical anion. The same signal was
seen in DMF. The splitting of 3.2 gauss is similar to that
reported in the literature for the radical anion generated
by alkali metal reduction in tetrahydrofuran or dimethoxy-
ethane (42).

Since relatively high concentrations of cycloheptatriene
and potassium $\underline{t}$-butoxide were necessary to generate the
radical, it was decided to check each component of the
reaction to rule out contaminants as the source of the
signal. Commercial cycloheptatriene from two different
companies was passed through silica gel and fractionally
distilled on a Todd column. A center cut from the

distillation still contained about three percent toluene
and one to two percent norbornadiene according to glpc
analysis. Material was then collected by glpc from
successive ODPN and SF 96 columns. These appeared to
remove all of the norbornadiene and most of the toluene.
Any remaining impurities were either much less than one
percent, or inseparable from cycloheptatriene on both
columns. Neither norbornadiene nor toluene gives any esr
signal under the conditions used. As a further check,
cycloheptatriene synthesized by reaction of crystalline
tropylium tetrafluoroborate and sodium borohydride
was tested and found to give the same esr signal.

The DMSO used in these experiments was commercial
material, distilled from calcium hydride and dried over
Molecular Sieves. Again, as a check, DMSO was prepared
by the pyrolysis of trimethylsulfoxonium iodide which
could be recrystallized to a high state of purity. The
same signal was seen using this material as solvent.

At least a threefold excess of potassium t-butoxide
must be used to generate the radical. When sufficient
base is used, a deep purple color develops in the solution.
The radical is only seen when the purple color is present,
but the purple color can be produced in other solvent-
base systems where no radical is seen. There is no signal
with potassium t-butoxide in DMF or in hexamethylphos-
phoramide (HMPA). Both sodium-potassium alloy in DMF

and sodium hydride in DMSO give a purple solution with cycloheptatriene, but give no radical. These observations suggest that the purple color is due to anion formation which is necessary but not sufficient for obtaining the radical. A previous report of formation of the anion with sodium-potassium alloy in tetrahydrofuran at -20° indicated that it was deep blue under those conditions (43). The radical is seen when cesium $\underline{t}$-butoxide is used as the base, but it is very short lived, disappearing in ten to fifteen minutes, while the radical formed with potassium $\underline{t}$-butoxide persists for several hours in the absence of air.

In summary, it appears that a moderately high concentration of cycloheptatriene and excess $\underline{t}$-butoxide in DMSO comprise a unique set of conditions for generation of this radical.

7-Deuterocycloheptatriene gives a spectrum identical to that from cycloheptatriene itself. When pure d_6-DMSO is used as the solvent, no signal is observed. In a 50-50 mixture of DMSO and d_6-DMSO a transient complex signal is produced which is different than the DMSO spectrum and may be due to a mixture of radicals. The signal disappears in a few minutes. It is possible that several partially deuterated species are being seen, and that the totally deuterated compound does not give an

observable radical. This is somewhat puzzling since
deuterium esr splittings are usually about one sixth the
magnitude of hydrogen splittings, and one sixth of the
larger splittings of 7 and 8 gauss in this radical would
still be greater than 1 gauss, and easily seen. The
rapid total exchange may indicate that the radical itself
is a highly delocalized anionic species, or that the
intermediate cycloheptatriene anion undergoes exchange
before going on to the radical.

The radical does not seem to be that of an isomer
of cycloheptatriene. Bicyclo[3.2.0]-hepta-2,5-diene was
prepared by photochemical isomerization (44). When it
was subjected to the esr conditions, no radical was
observed. The [4.1.0] isomer, norcaradiene, is highly
unstable except in certain substituted cases, and its
formation or existence in the present conditions seems
unlikely. Also it would be expected to give a more
symmetrical radical than the one observed.

Another possibility is that the radical results from
some type of reaction between cycloheptatriene and
dimethyl sulfoxide. The dimethyloxosulfonium methylide
has been used as a methylene transfer agent with
unsaturated ketones (45). The same type of addition
to cycloheptatriene could give two bicyclo[5.1.0]-
octadienes, with the following structures:
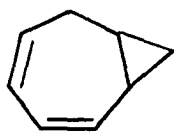
bicyclo-[5.1.0]-2,4-octadiene   bicyclo[5.1.0]-2,5-octadiene
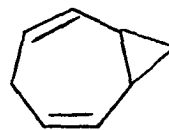
When cycloheptatriene was reacted with Simmons-Smith
reagent, six product peaks were observed by glpc. It
had previously been reported that reaction with
diazomethane yielded mono-, di- and tricyclopropanated
compounds (46). The first two product peaks were assumed
to be from mono-adducts and samples of them were collected.
With excess t-butoxide in DMSO, the first gave no signal,
while the second gave a spectrum identical with that
from cyclooctatetraene. Doering had observed the
following isomerizations (46):
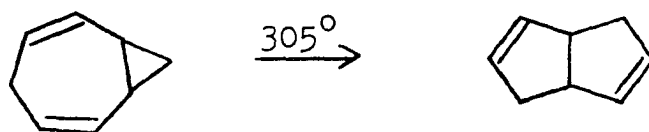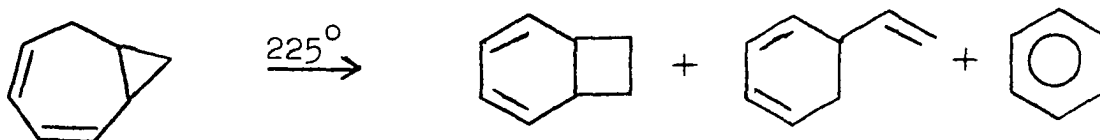
The products in the first reaction could result from an
initial transformation to cyclooctatriene. It is possible
that this type of isomerization of the Simmons-Smith
product had occurred in the glpc, and that the strong
base generated the cyclooctatetraene radical anion from
cyclooctatriene or from the bicyclic isomer itself. Simple
insertion by the Simmons-Smith reagent is unlikely.

Oxygenation by DMSO is another conceivable type of
reaction that could result in a ketyl, semidione, or
semiquinone species such as those below:
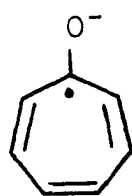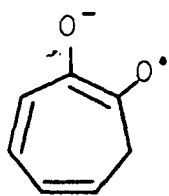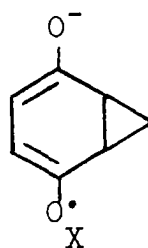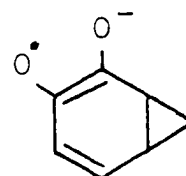
| VIII | IX | X | XI |

VIII is another system that would be expected to give a
symmetrical esr spectrum. A spectrum showing three
equivalent pairs of protons, and probably due to VIII,
is reported in Weiner's thesis (27). As previously
mentioned, no radical could be observed when reduction
of tropone or tropolone with sodium-potassium alloy
was attempted in the esr cell. IX is a semidione which
might be formed by oxidation of 2,4-cycloheptadienone.
An isomer of this compound, bicyclo-[4.1.0]-3-hepten-2-one

or norcarenone, could oxidize to the semiquinone X. This
ketone has reportedly been isolated from carefully
controlled solvolysis of tosylate VI (47). The end product
of the solvolysis is the dienone. Again, the symmetry

XII
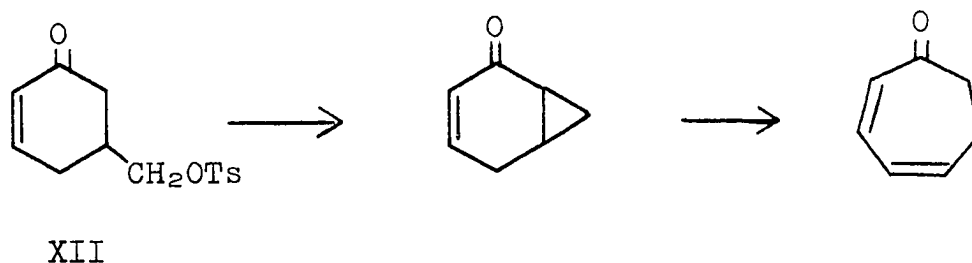
of X makes it a less likely choice for the mystery
radical than IX or XI, both of which have the requisite
six non-equivalent hydrogens. However, neither parent
ketone of XI has ever been isolated.

2,4-Cycloheptadienone was prepared and reacted with
potassium t-butoxide in DMSO. The mixture gave no esr
signal, with or without added oxygen. To check the
intermediacy of X or XI, the tosylate XII was reacted
with excess t-butoxide in DMSO, and with dilute potassium
hydroxide, in the esr cell. Again there was no detectable
radical produced. Base caused rapid darkening and
polymerization of the dienone. Samples of the isomeric
4,5-trimethylene-2,4- and 2,5-cycloheptadienones were
available. These also failed to give any esr signal with
excess t-butoxide in DMSO.

Another probe of radical structure is substitution.

Thus, the 7-methyl-, 7-ethyl-, 7-isopropyl-, 7-methoxy-, 3-methoxy-, and 3,7,7-trimethylcycloheptatrienes were prepared. All failed to give esr spectra with excess t-butoxide in DMSO. Alkyl or alkoxy substitution would be expected to make anion formation more difficult and disubstitution at the 7-position makes it impossible. This is another indication that an anion is a precursor to the radical.

The 7- and 3-phenylcycloheptatrienes gave strong, identical esr signals with excess potassium t-butoxide in DMSO. However, these did not appear to be related to the cycloheptatriene radical. The major splitting pattern was due to two pairs of protons with hfsc 5.2 and 2.6 gauss, with at least 5 smaller splittings. It may be that the phenyl substitution gives sufficient stability to the radical anion to allow it to be generated under these conditions. The previously reported cycloheptatriene radical anion was formed via electrolysis in liquid ammonia at -78°.

Quenching of the phenylcycloheptatriene esr sample with deuterium oxide, followed by mass spectral analysis, indicated some deuterium incorporation. Comparison of a mass spectrum of the starting material with that from the esr sample also indicated that a considerable amount of a species with the molecular weight of biphenyl (154) was

formed during the reaction. The intensity of this peak
in the spectrum of the starting material was about one
fourth the intensity of the molecule ion (168). Glpc
indicated that two to three percent of biphenyl was
present in the starting material. In the spectrum of
the esr residue the 154 peak was twenty times as intense
as the one at 168. Although splittings of 5.2 and 2.6
gauss are seen in the biphenyl radical anion, it could not
be generated under the present conditions. This unusual
side reaction may not be related to the formation of
the radical anion that was observed from the phenylcyclo-
heptatrienes.

In conclusion, the following negative statements
can be made about the mystery radical:

(1) Monocyclic structures VIII, IX and XIII through
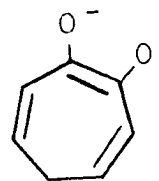XVIII can be excluded.
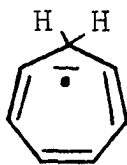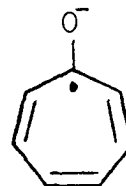
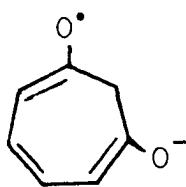XIII   XIV   VIII
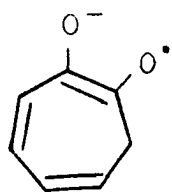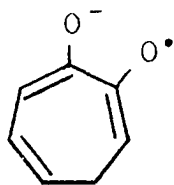
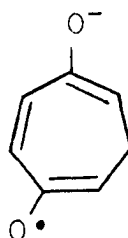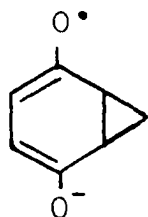IX   XV   XVI

XVII   XVIII

(2) Bicyclic structures in the [4.1.0] system, such
as **X**, **XI**, **XIX**, **XX** and **XXI** can be excluded.
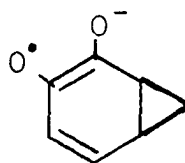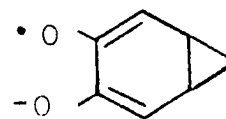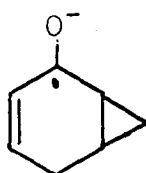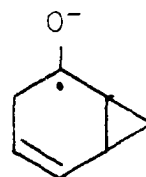
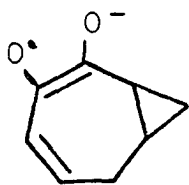X   XI   XIX

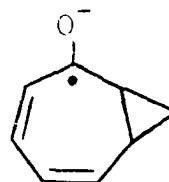XX   XXI

(3) Bicyclo [5.1.0] octane structures XXII and XXIII
can be excluded.

XXII   XXIII

(4) One could imagine a sequence of conversion such
as the following, leading to bicyclo [3.2.0] heptanes.

    or
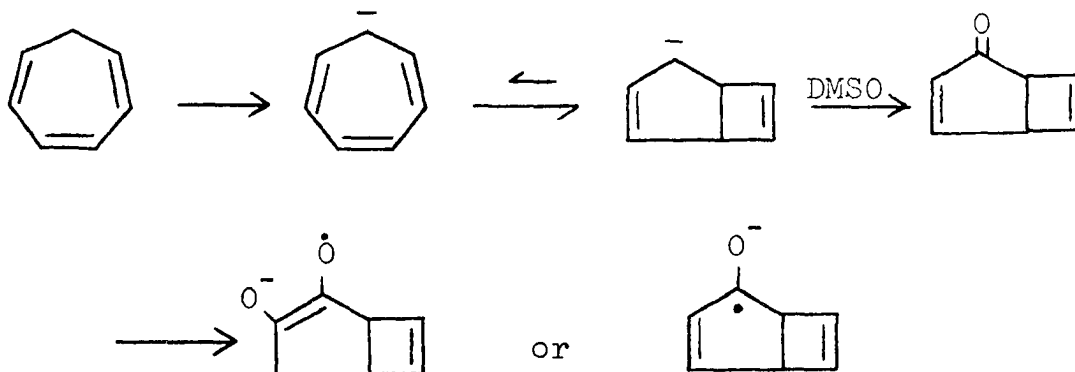
However, the fact that the bicyclo[3.2.0]heptadiene does not give any signal makes it unlikely that this sequence proceeds through the oxygenation.

Finally, a ketyl or hydrocarbon radical anion structure seems more probable than a semidione or semiquinone, since oxygen is not required to form the mystery radical, and, in fact, traces of oxygen rapidly destroy it.

ESR SPECTRA

Figure 1. First derivative esr spectrum of $\underline{o}$-naphthosemiquinone radical
anion (Radical A) prepared by reduction of the quinone with
propiophenone anion in potassium $\underline{t}$-butoxide-DMSO.

GAUSS
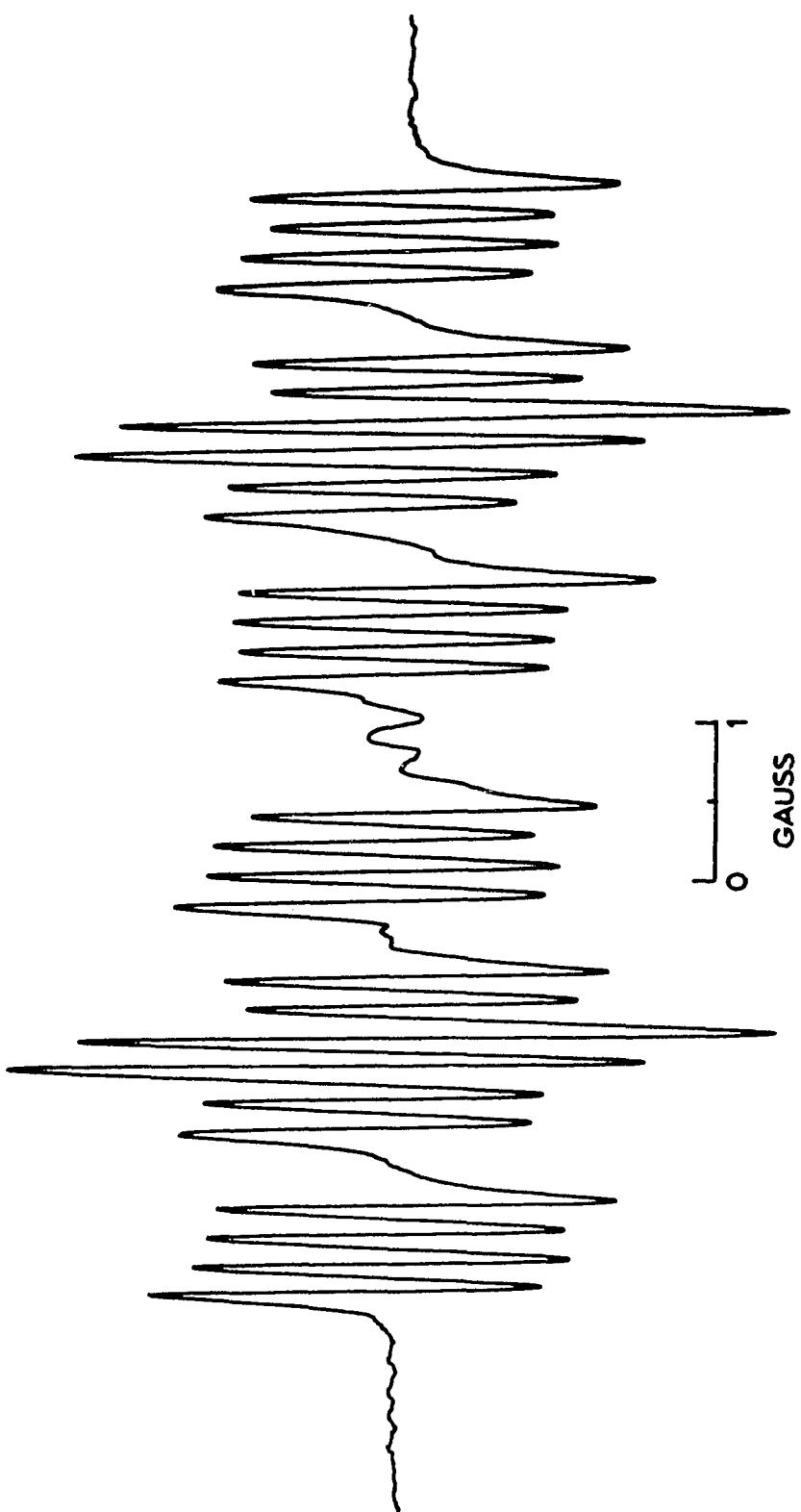
Figure 2. First derivative esr spectrum of radical anion (Radical B) formed
by 2-hydroxy-1,4-naphthoquinone (lawsone) with propiophenone
anion in potassium t-butoxide-DMSO.
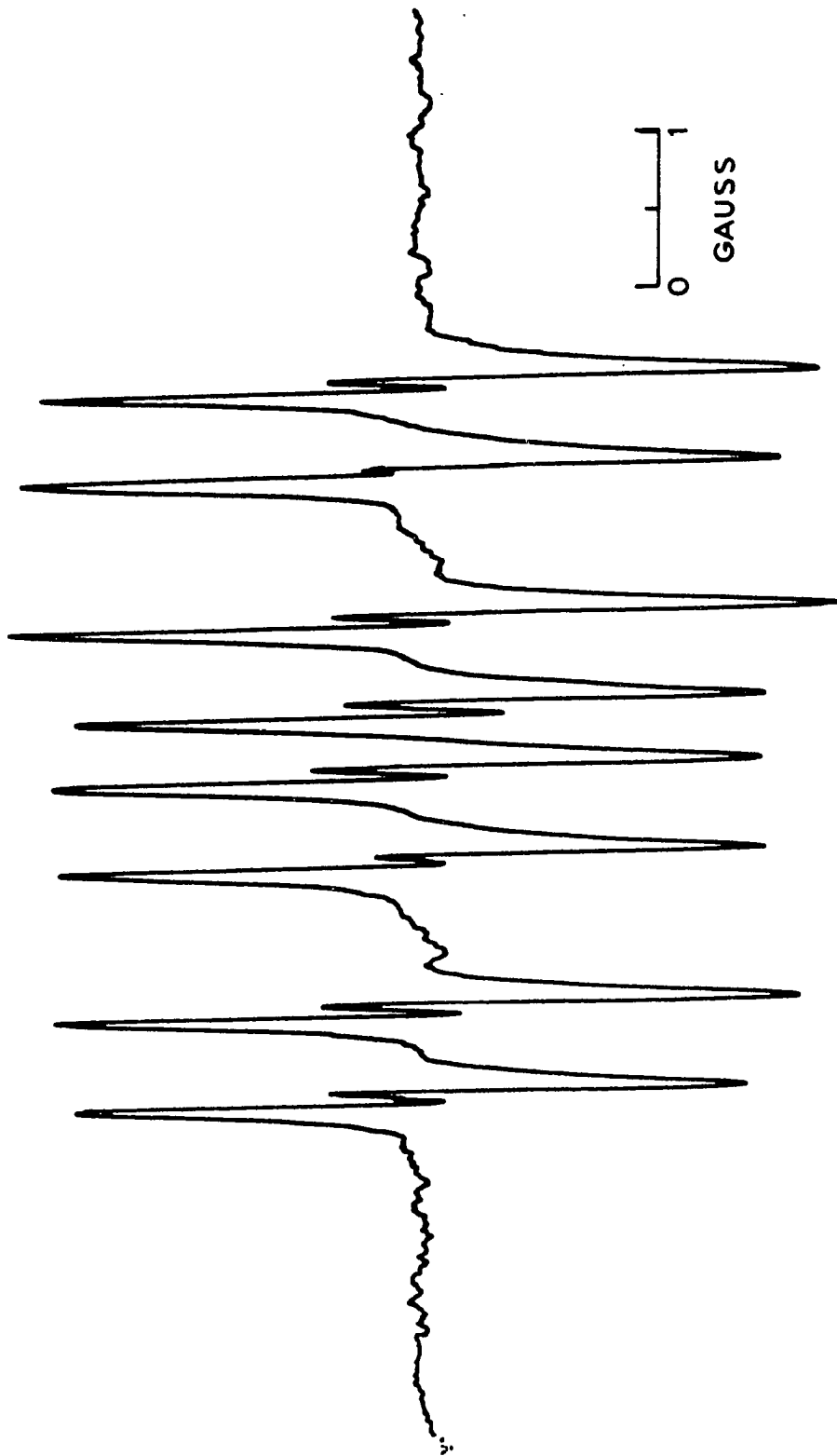
Figure 3. First derivative esr spectrum of initial radical seen when air is added to a solution of $\underline{\beta}$-tetralone in potassium $\underline{t}$-butoxide-DMSO.
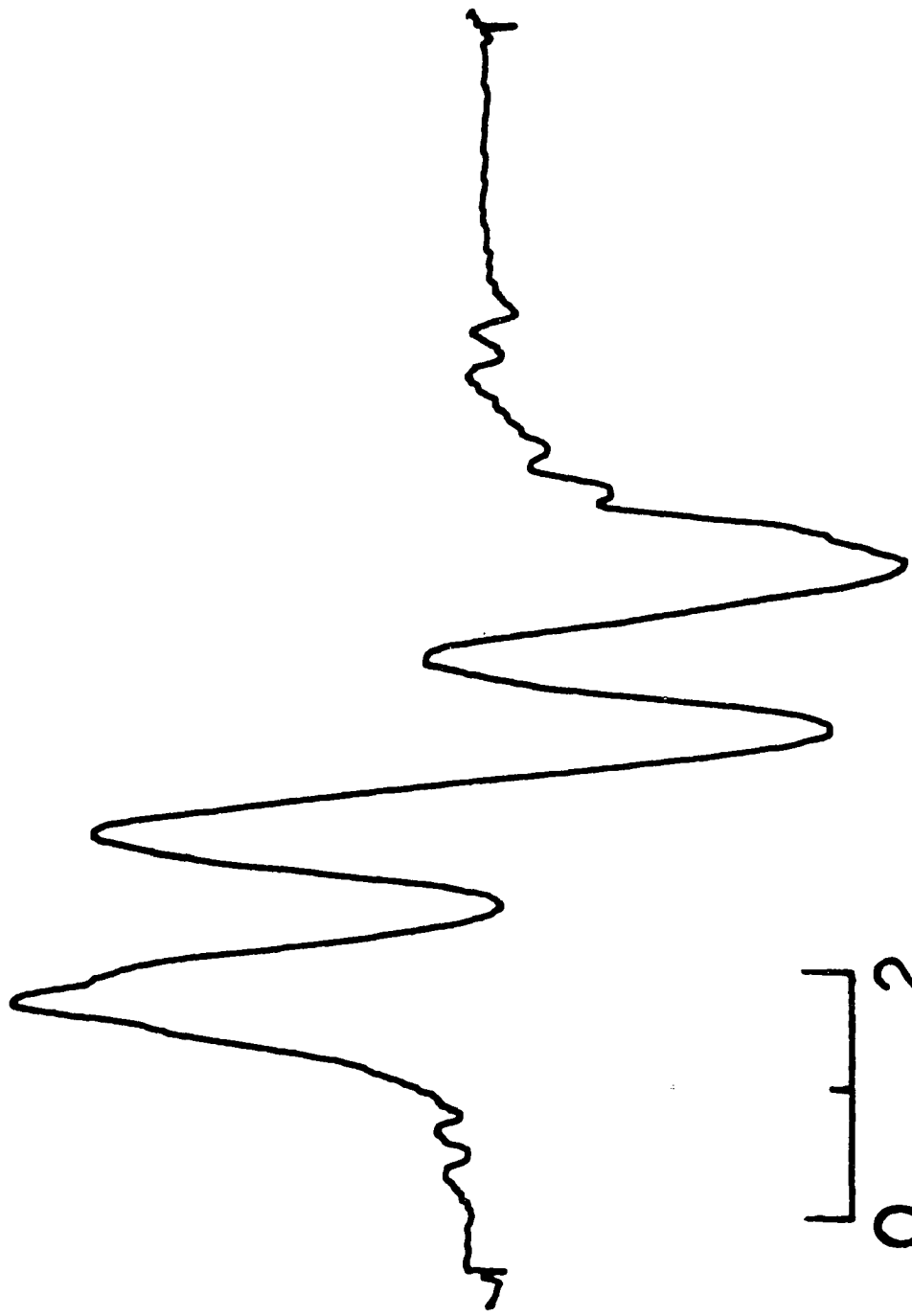
GAUSS

Figure 4. First derivative esr spectrum of radical from 3-methyl-2-hydroxy-
1,4-naphthoquinone (phthiocol) with propiophenone anion in
potassium t-butoxide-DMSO.
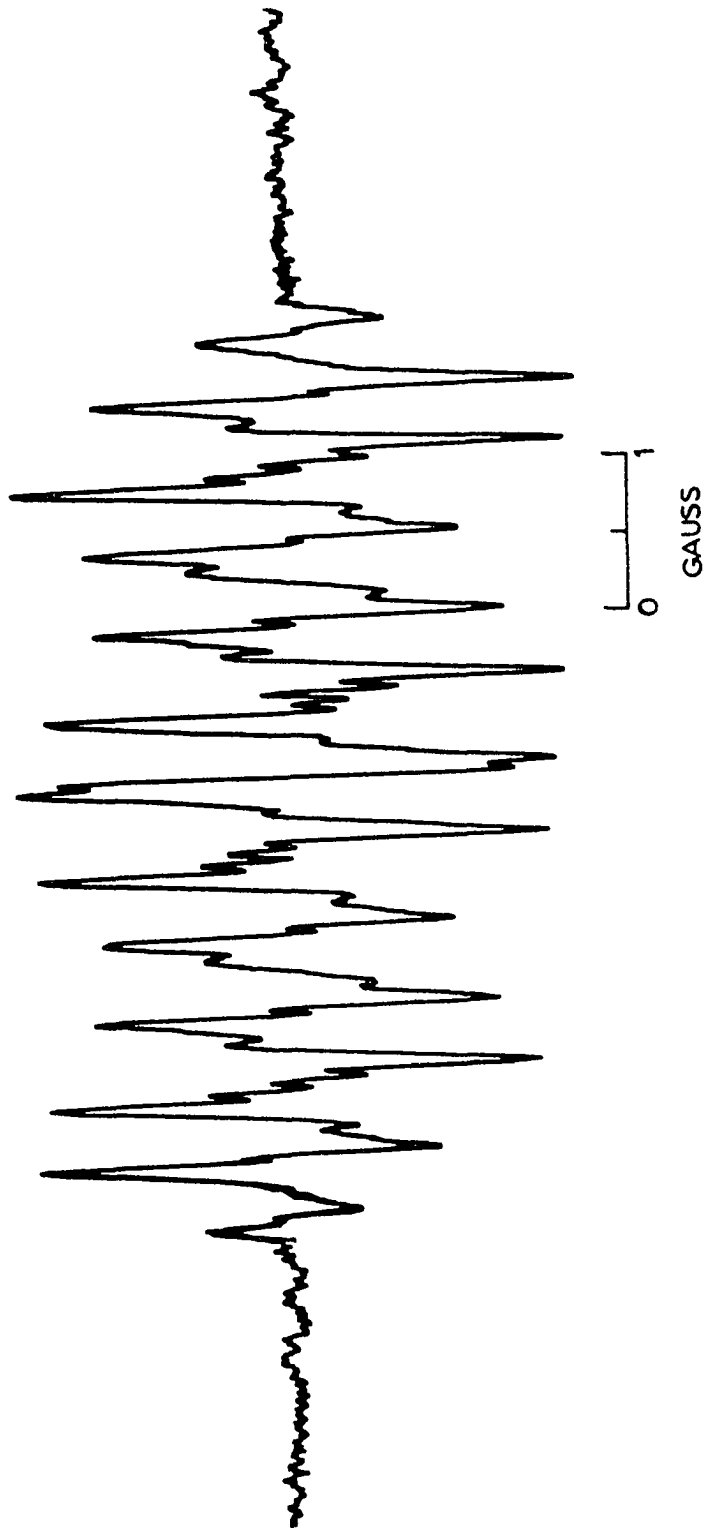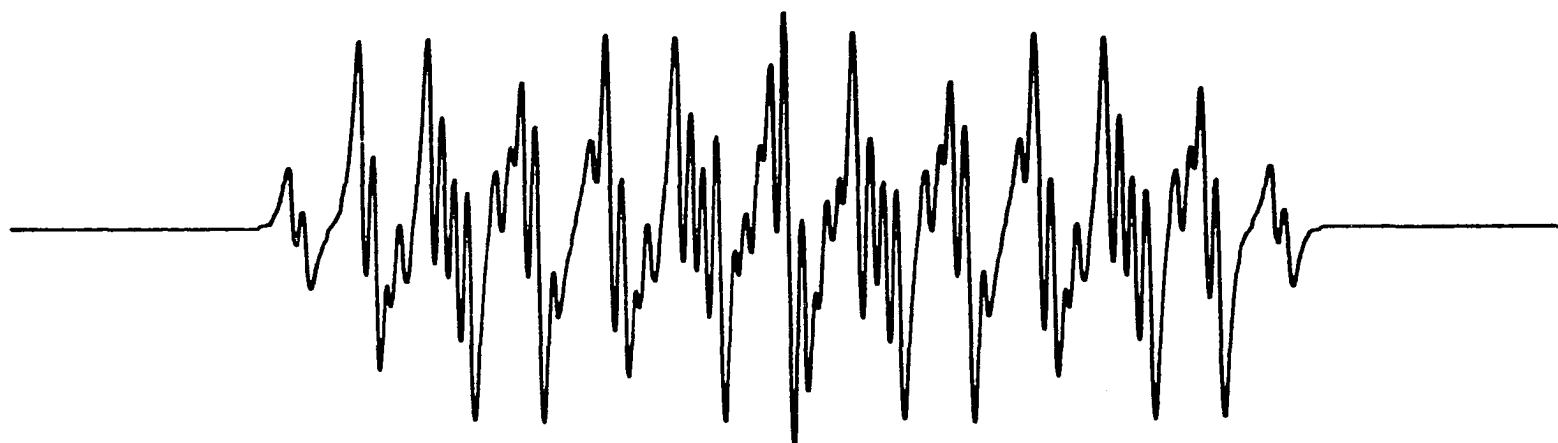
GAUSS

Figure 5. Simulated esr spectrum for Lorentzian line width of 0.1 gauss and hfsc
from text for phthiocol in potassium t-butoxide-DMSO, performed by
JEOLCO JNM-RA-1 spectrum accumulator.

Figure 6. First derivative esr spectrum of radical formed on addition of
air to a solution of 4-methyl-1-tetralone in potassium t-butoxide-
DMSO.

GAUSS

Figure 7. Simulated esr spectrum for Lorentzian linewidth of 0.1 gauss and hfsc from text for 4-methyl-1,2-naphthoquinone radical anion, performed by JEOLCO JNM-RA-1 spectrum accumulator.

Figure 8. First derivative esr spectrum of initial radical formed on addition
of air to a solution of 5-methoxy-1-tetralone in potassium $\underline{t}$-butoxide-
DMSO.

GAUSS
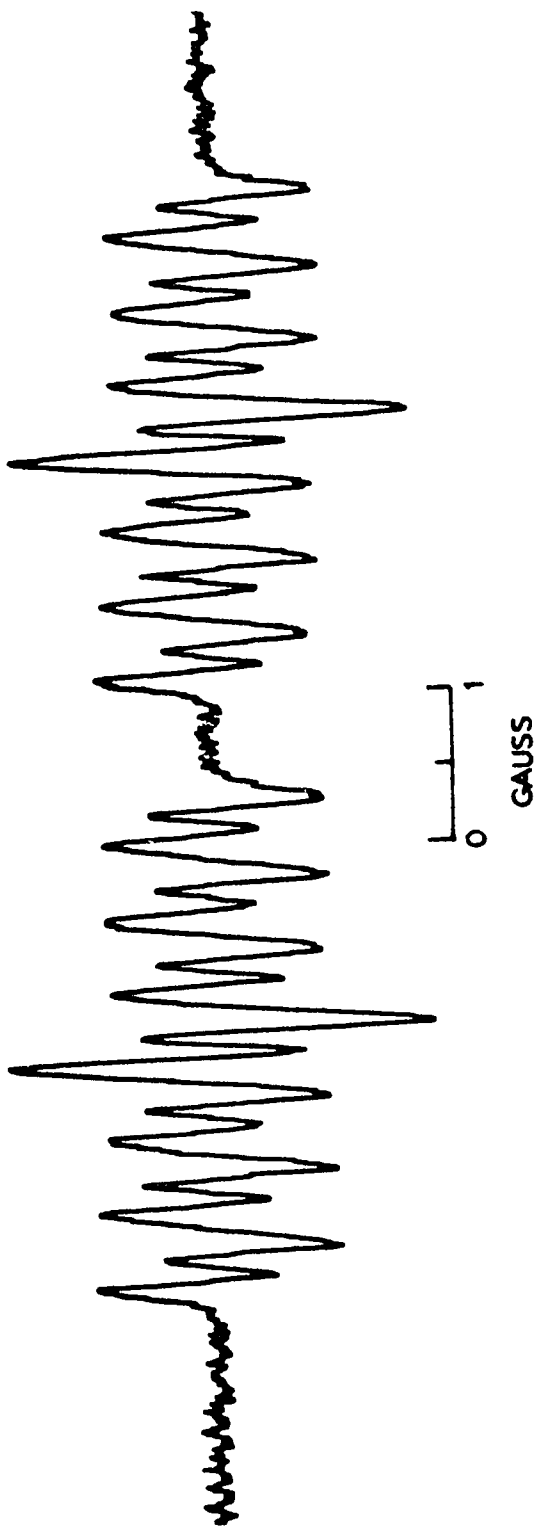
Figure 9. First derivative esr spectrum of radical anion formed by reduction of 2-hydroxy-5-methoxy-1,4-naphthoquinone with propiophenone anion in potassium t-butoxide-DMSO.

GAUSS
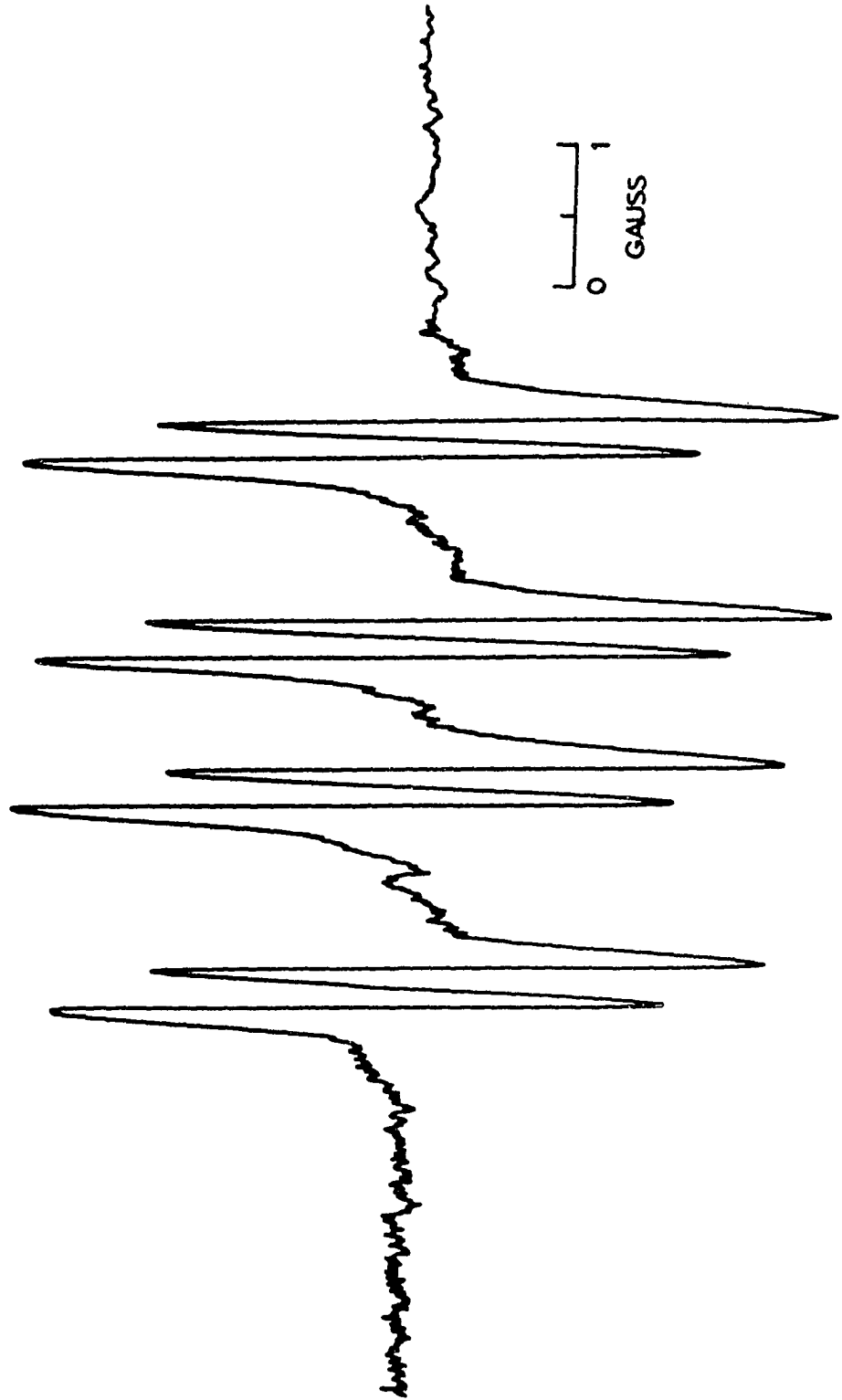
Figure 10. First derivative esr spectrum of initial radical formed on addition
of air to a solution of 6-methoxy-1-tetralone in potassium
t-butoxide-DMSO.

GAUSS
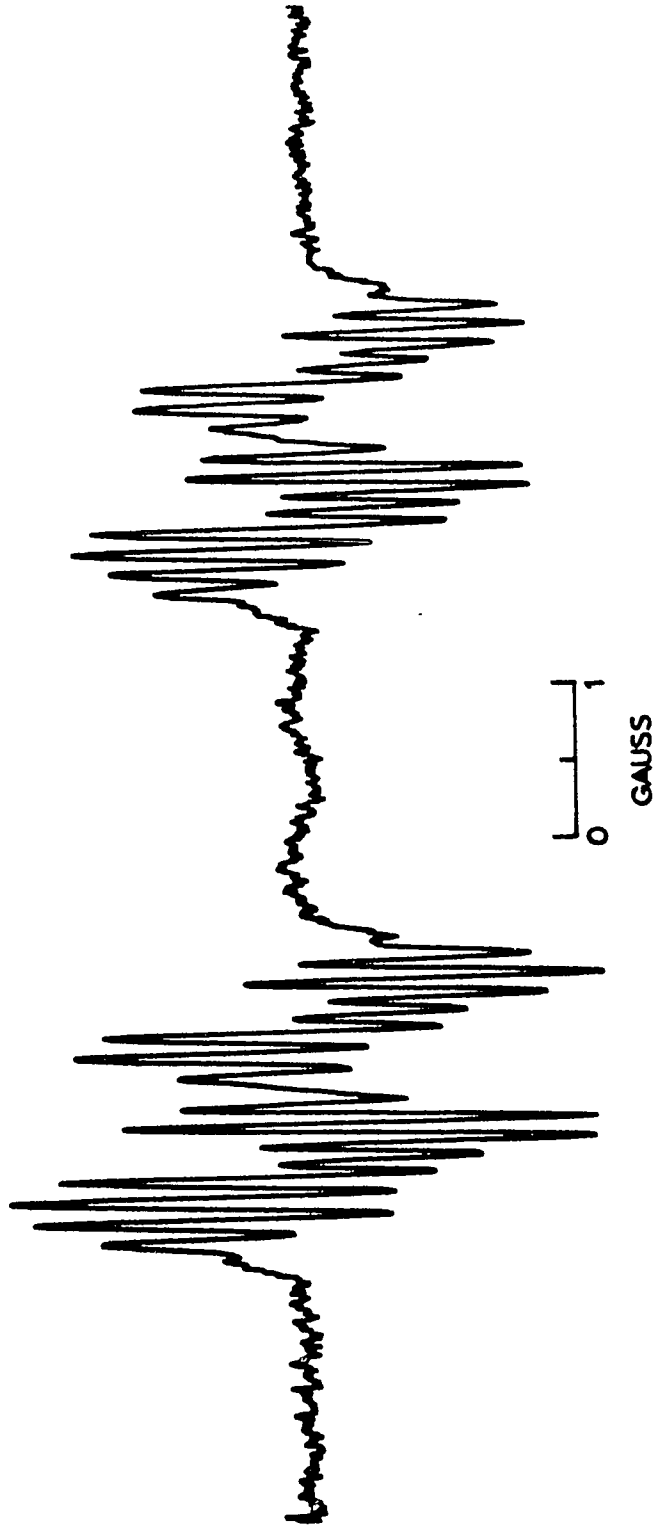
Figure 11. First derivative esr spectrum of radical eighteen hours after

addition of air to a solution of 6-methoxy-1-tetralone in

potassium t-butoxide-DMSO.

GAUSS
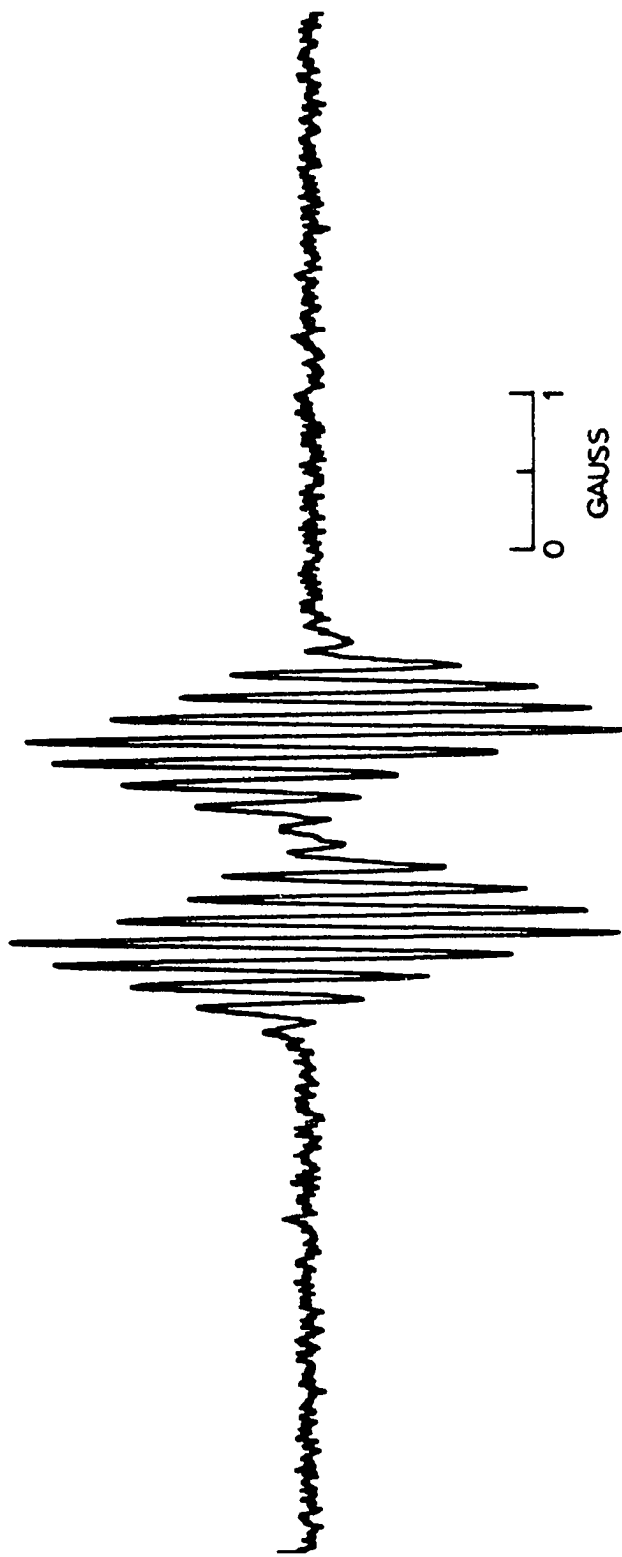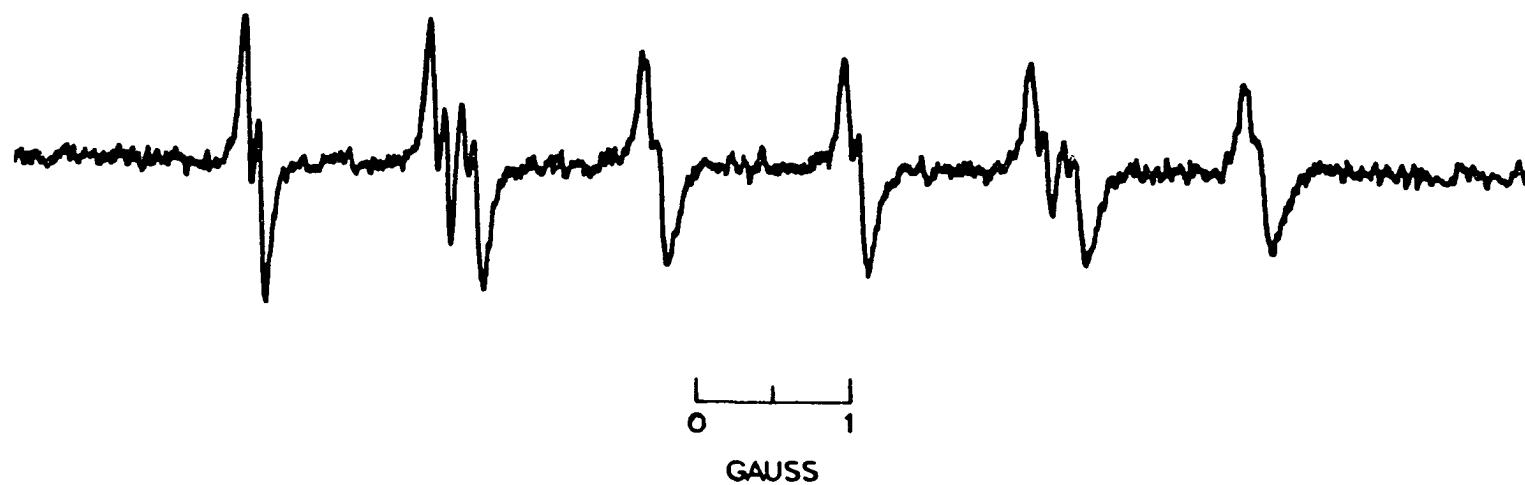
Figure 12. First derivative esr spectrum of initial radical formed on addition of air to a solution of 7-methoxy-1-tetralone in potassium t-butoxide-DMSO.
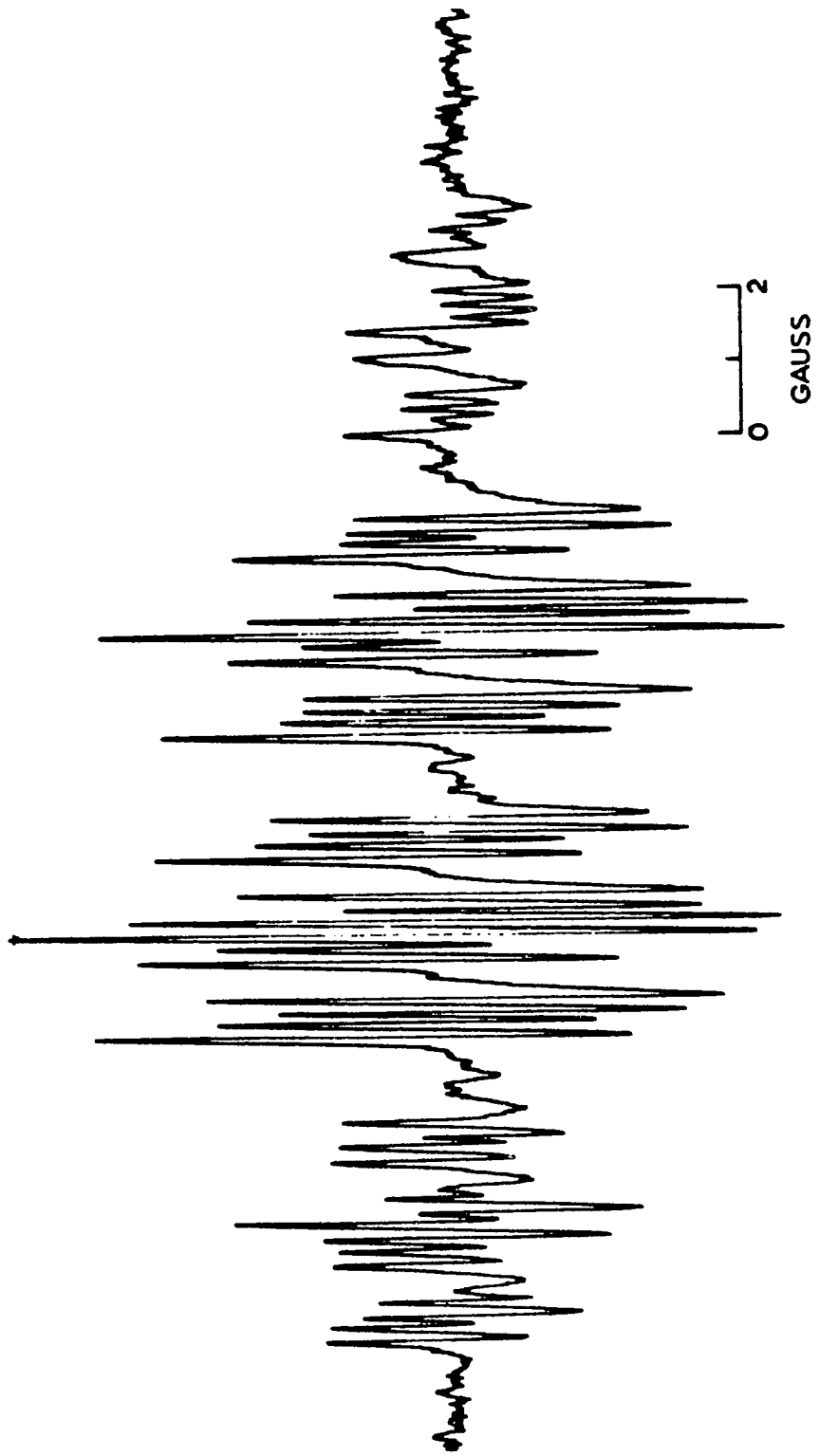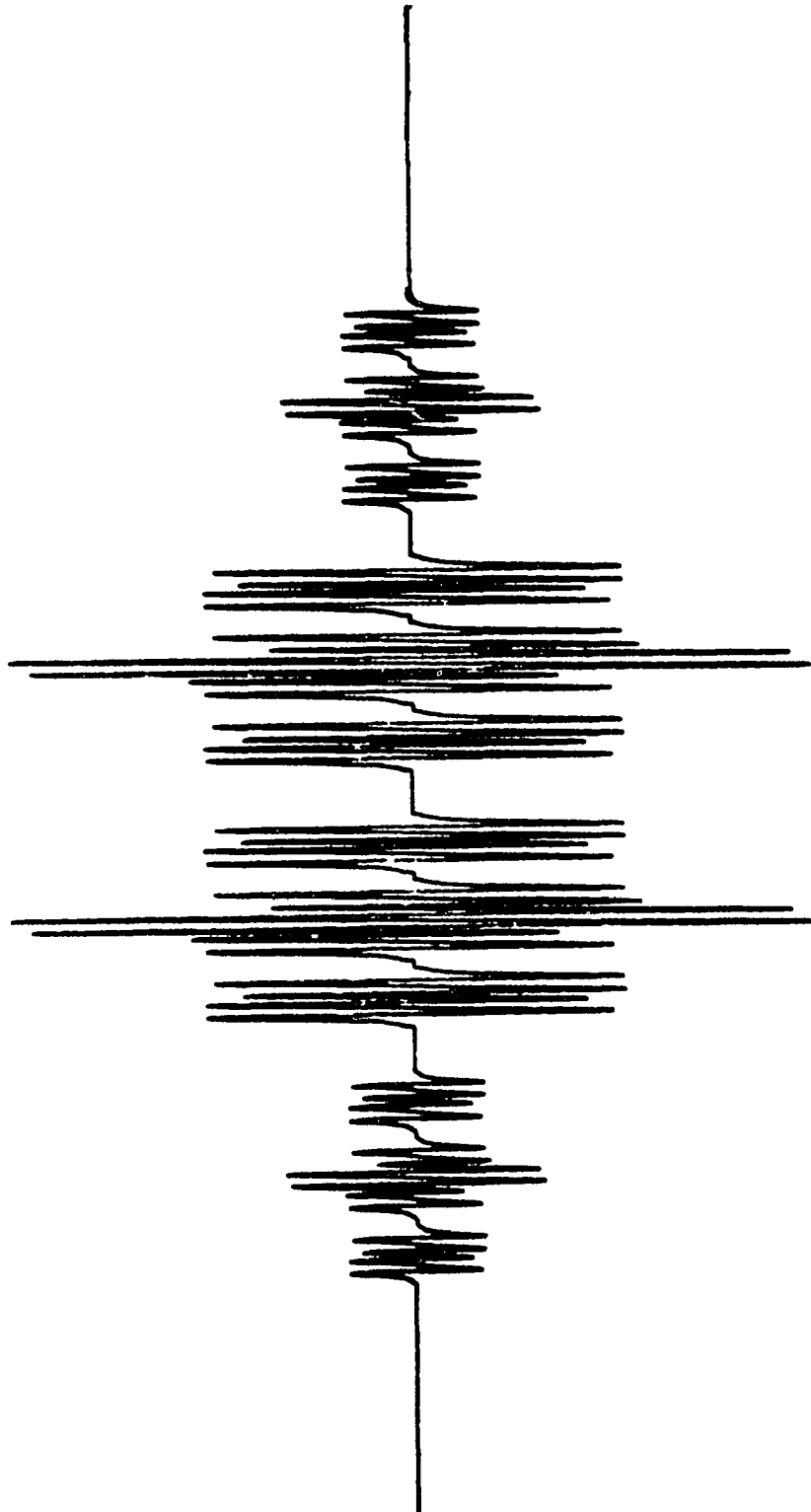
Figure 13. First derivative esr spectrum of radical sixteen hours after the addition of air to a solution of 7-methoxy-1-tetralone in potassium t-butoxide-DMSO.

GAUSS
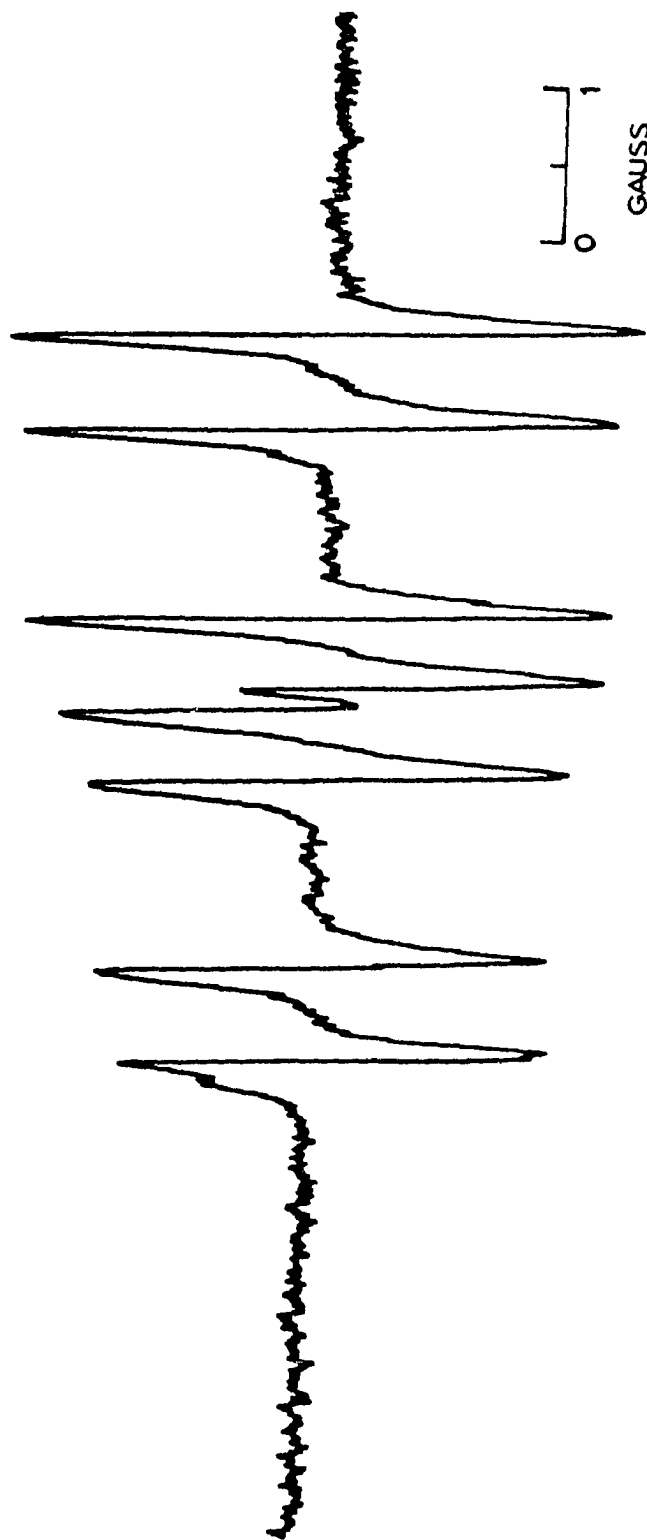
Figure 14. First derivative esr spectrum of radical from reduction of 2-hydroxy-1,4-naphthoquinone (lawsone) with propiophenone in 0.1 N potassium hydroxide.

GAUSS
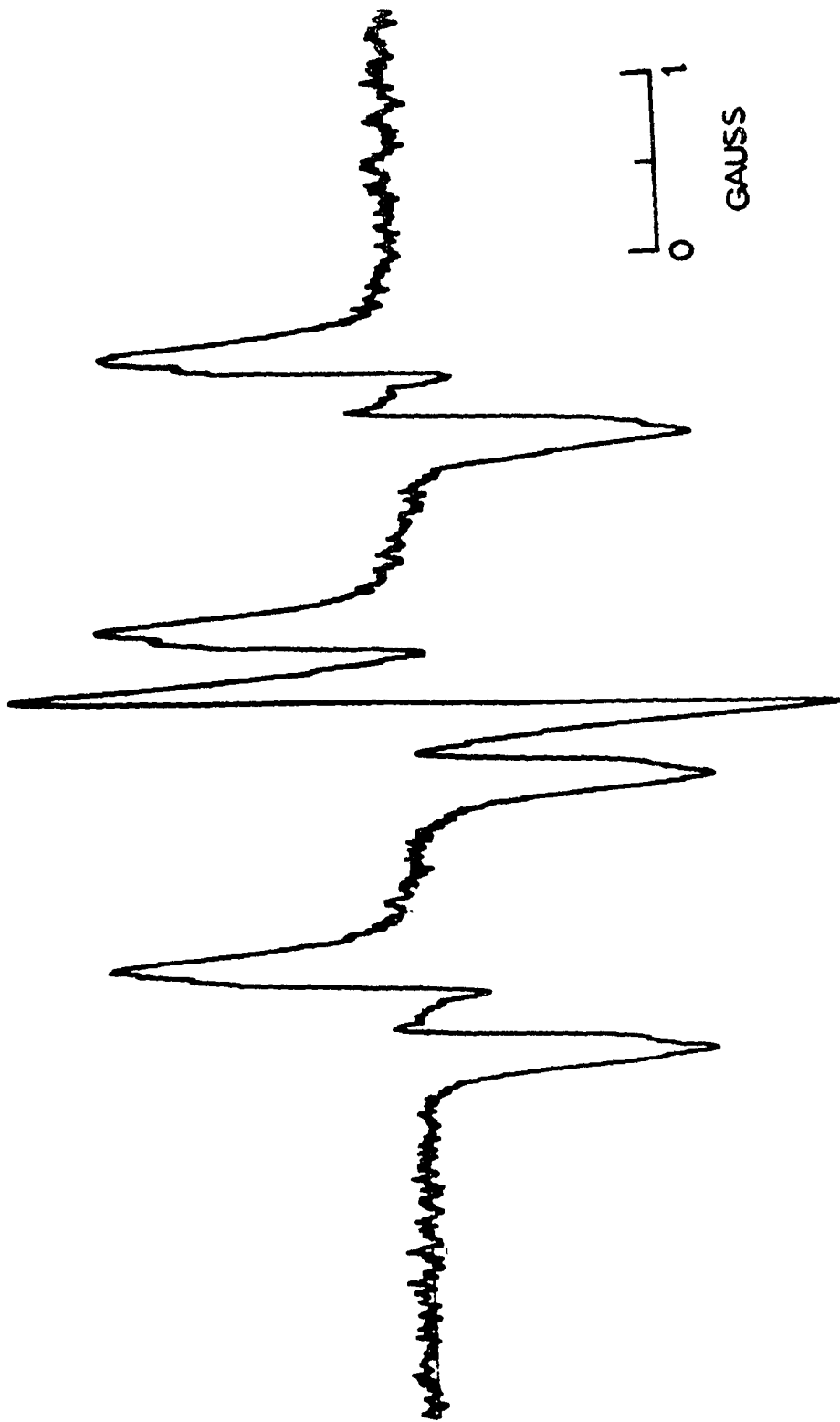
Figure 15. First derivative esr spectrum of radical from reduction of

2-hydroxy-1,4-naphthoquinone (lawsone) with propiophenone

and potassium t-butoxide in 80% t-butyl alcohol-20% water.

GAUSS

1

0
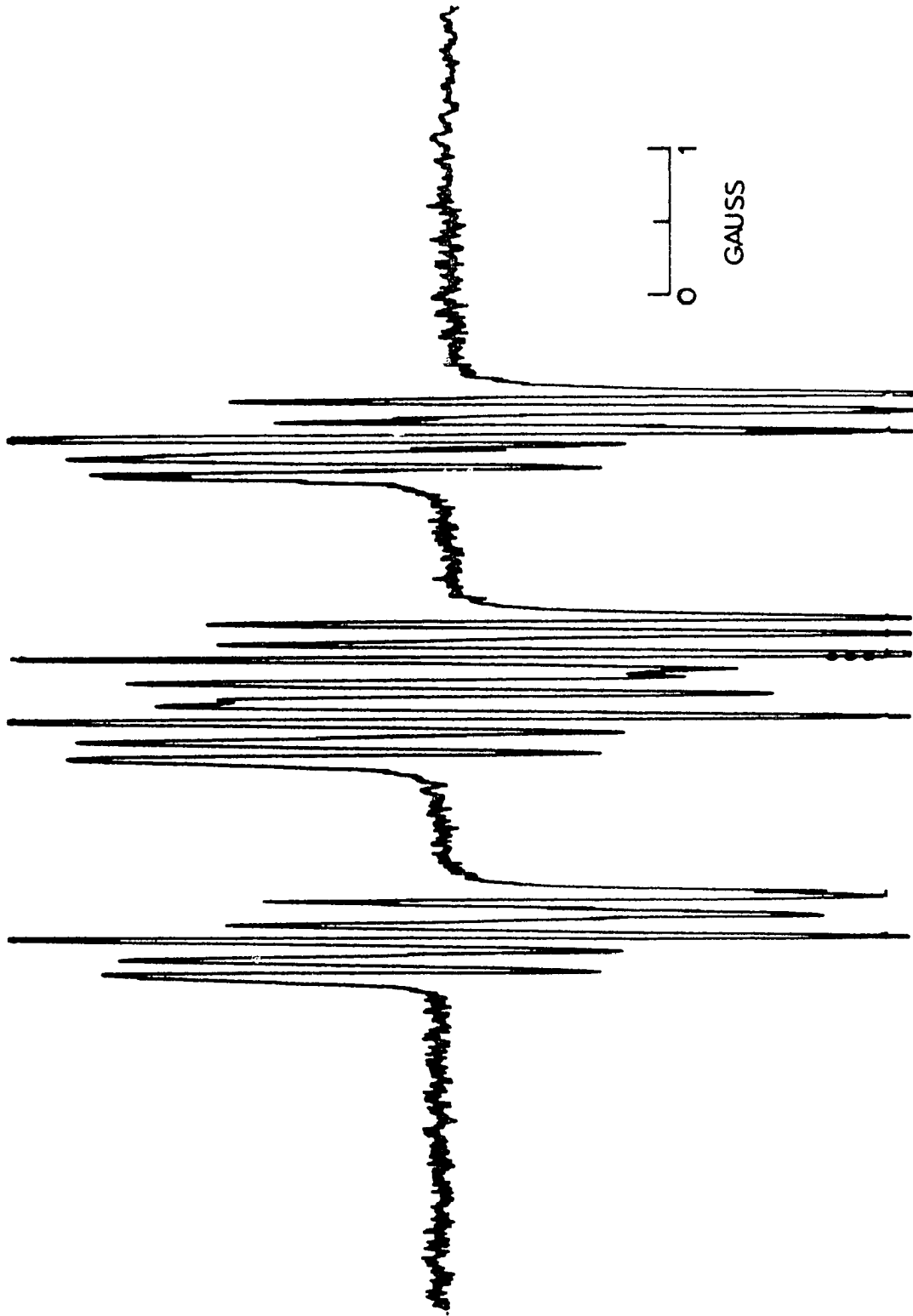
Figure 16. First derivative esr spectrum of radical from reduction of

3-methyl-2-hydroxy-1,4-naphthoquinone (phthiocol) with

propiophenone in 0.1 N potassium hydroxide.

GAUSS

0   1
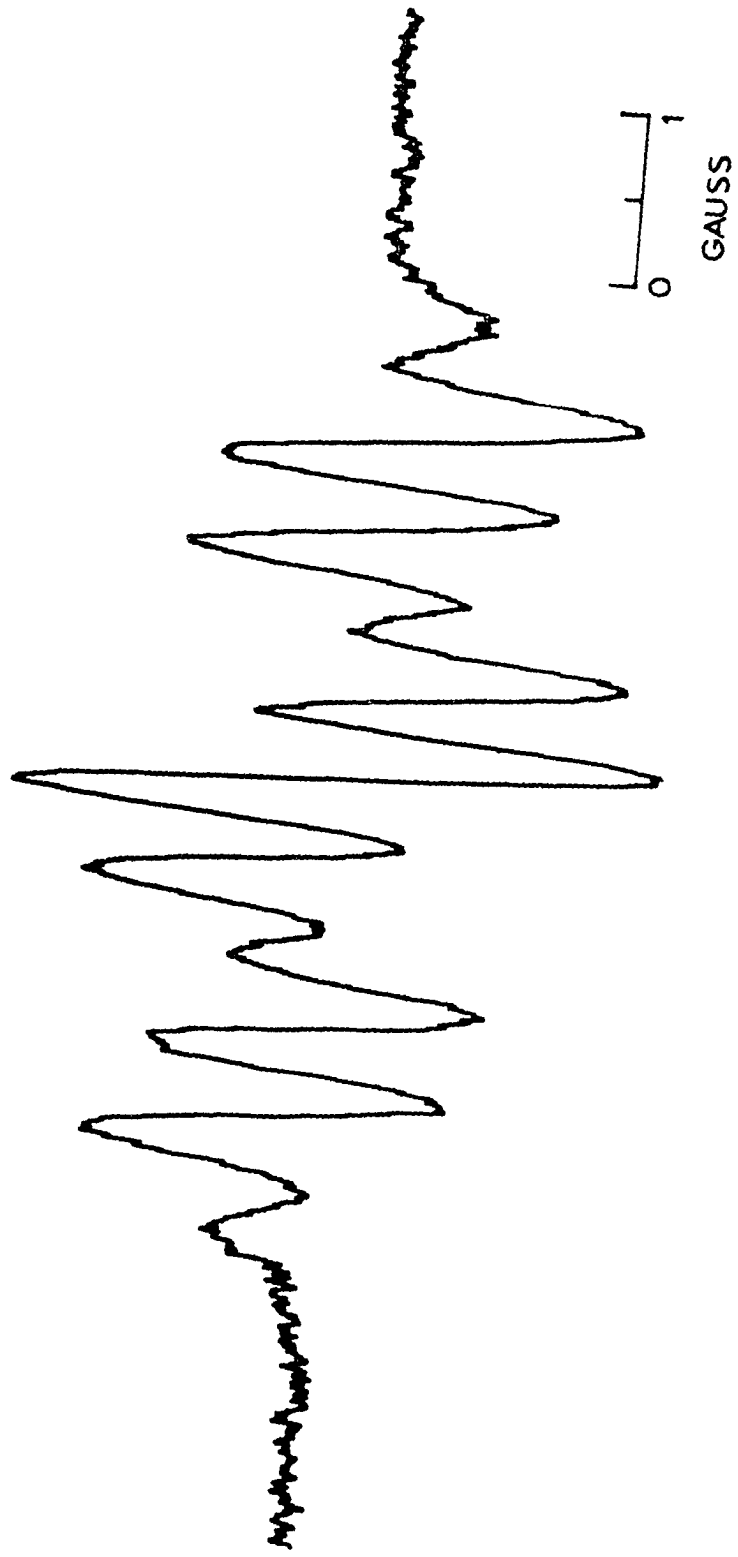
Figure 17. First derivative esr spectrum of radical or mixture of radicals

formed by the Wichelhaus oxide in potassium t-butoxide-DMSO.

GAUSS
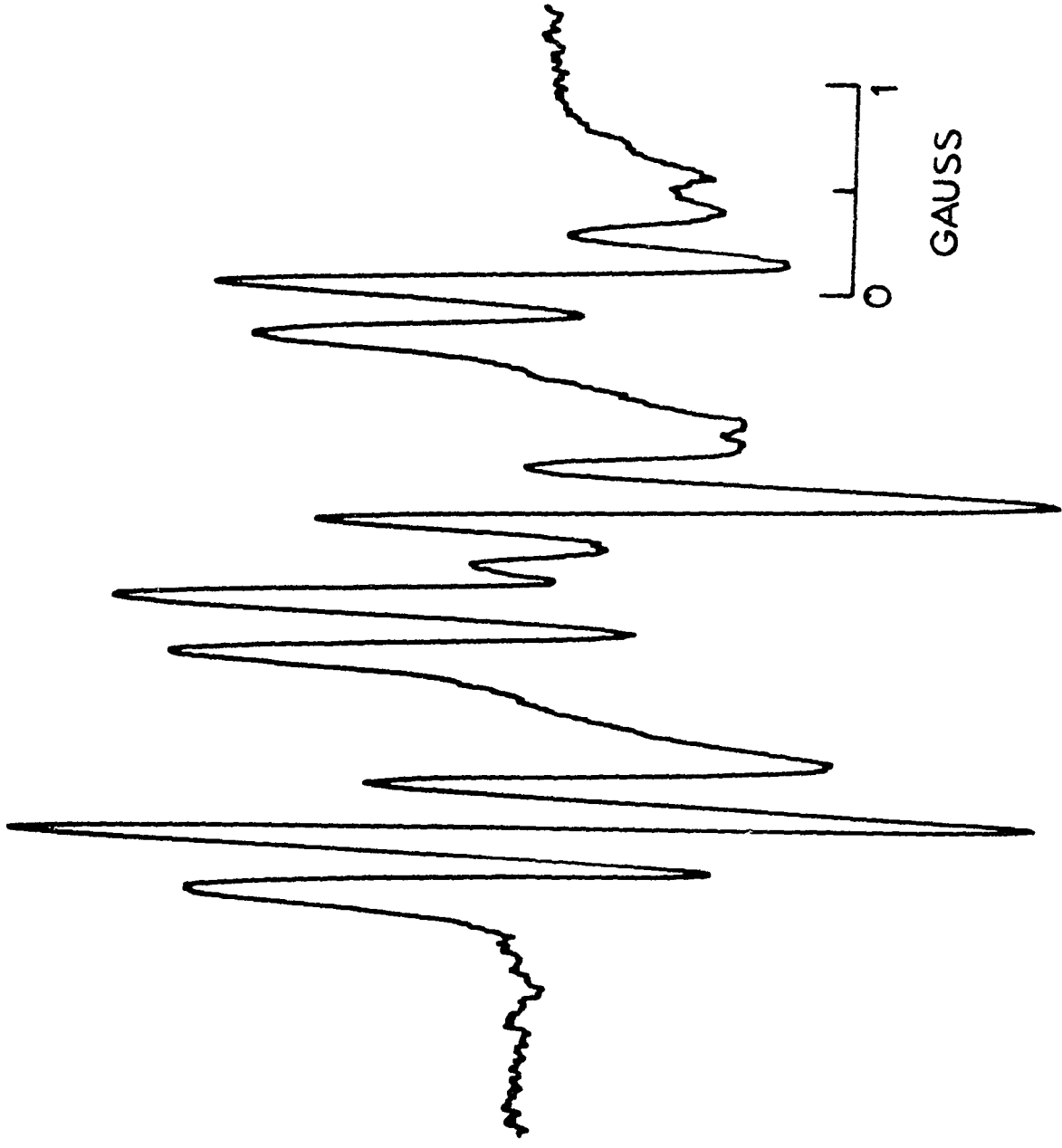
Figure 18. First derivative esr spectrum of radical formed by 2,5-dihydroxy-1,4-naphthoquinone (juglone) in potassium t-butoxide-DMSO in the absence of oxygen.
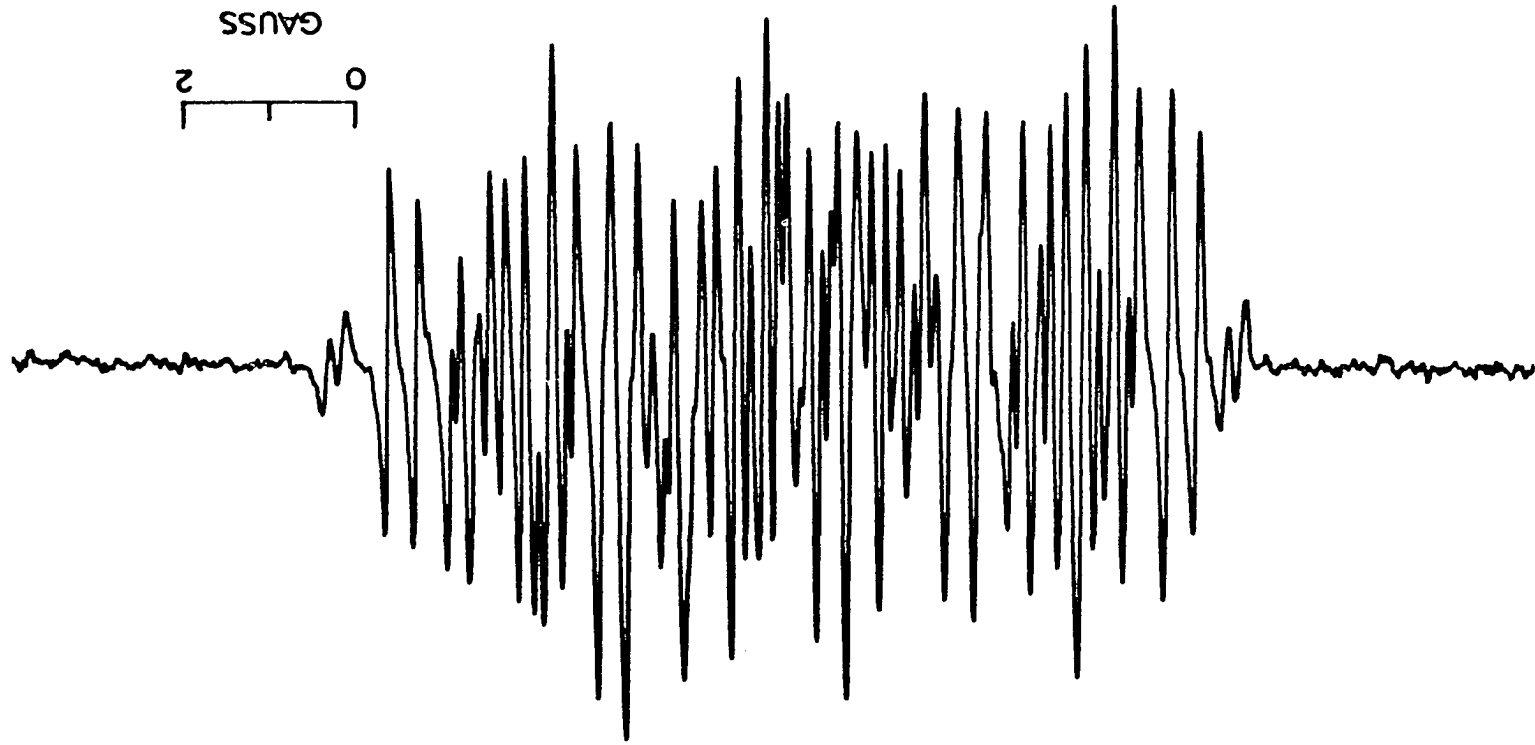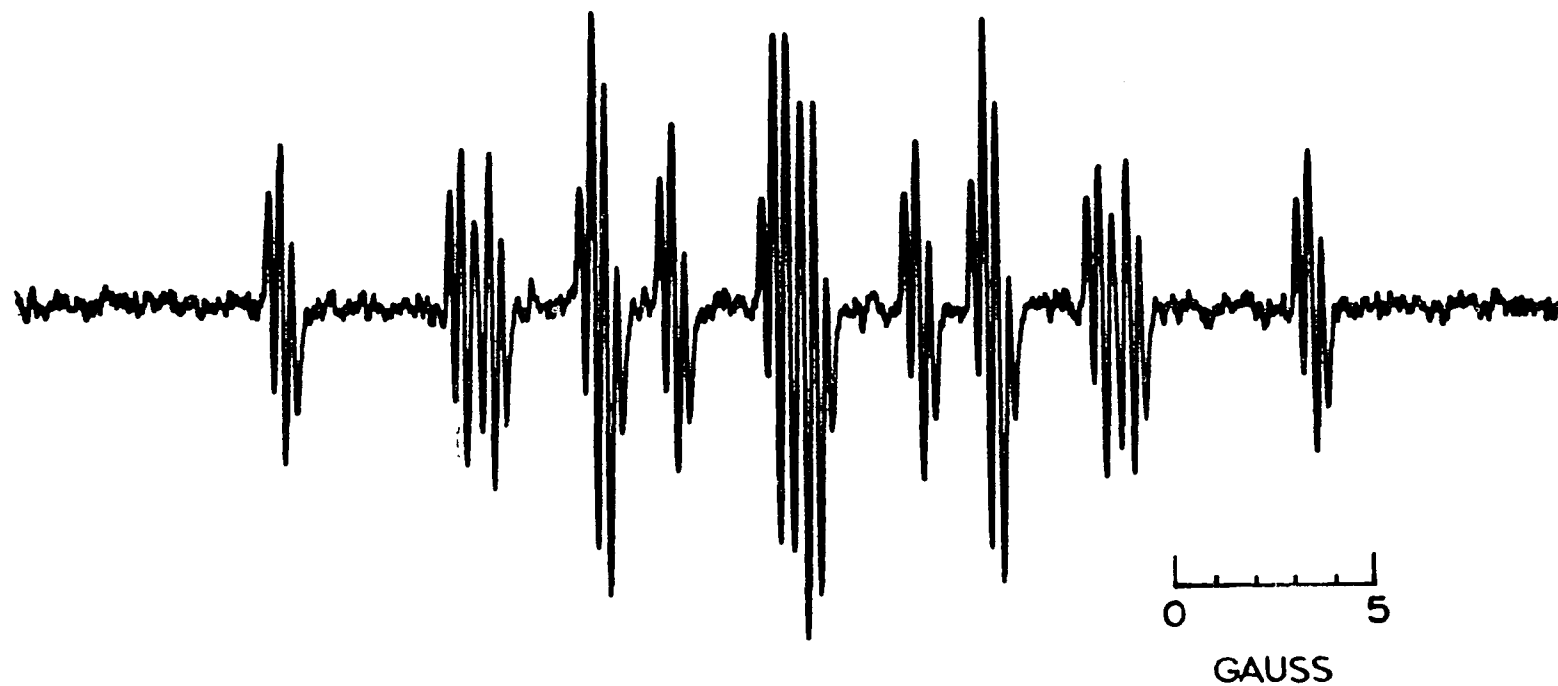
Figure 19. First derivative esr spectrum of the mystery radical prepared from cycloheptatriene and excess potassium t-butoxide in DMSO.

Figure 20. First derivative esr spectrum of radical from cycloheptatriene and

excess potassium $\underline{t}$-butoxide in a 1:1 mixture of DMSO and d_6-DMSO,

twenty minutes after mixing.
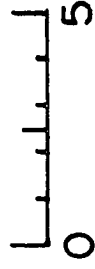
GAUSS
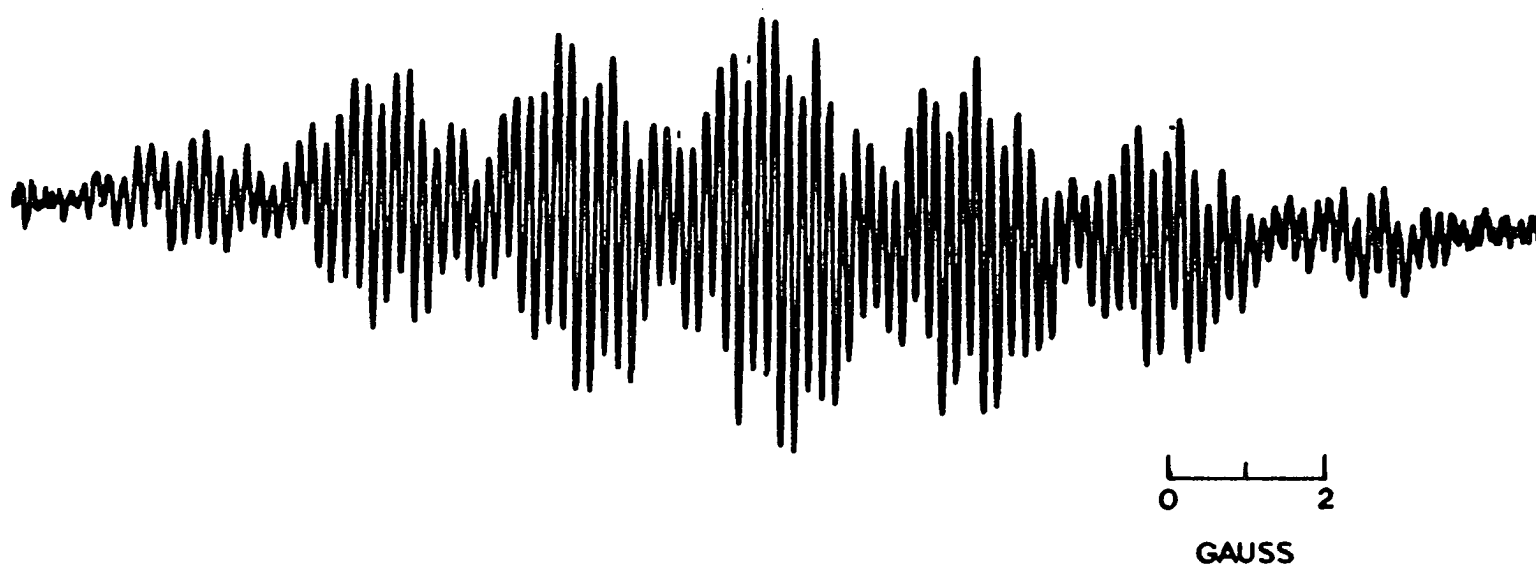
Figure 21. First derivative esr spectrum of radical prepared from 7-phenyl-cycloheptatriene with excess potassium t-butoxide in DMSO.

Figure 22. First derivative esr spectrum of radical prepared by addition of
air to a solution of (a) 7,8,9-trimethoxybenzocycloheptene-1-one
in potassium t-butoxide-DMSO; (b) 2,7,8-trimethoxy-9-hydroxy-
benzocycloheptene-1-one in potassium t-butoxide-DMSO.

(a)

0   2

GAUSS

(b)

0   5

GAUSS
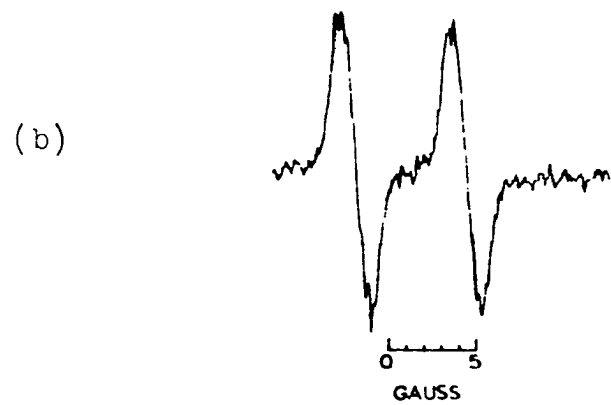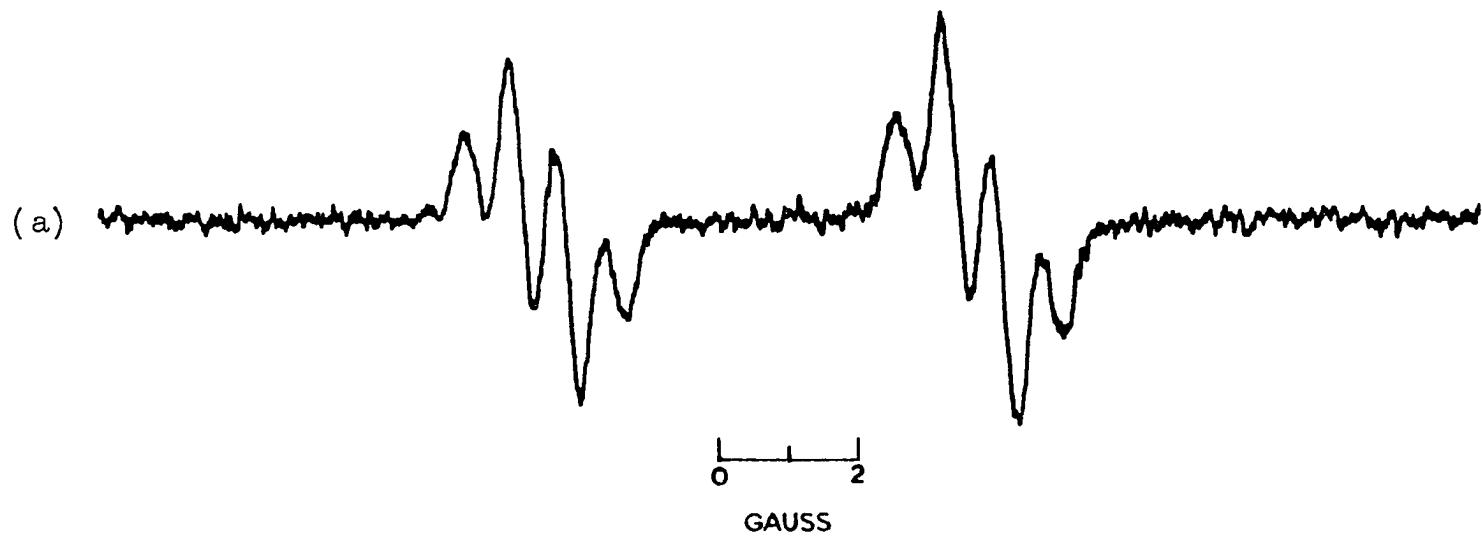
Figure 23. First derivative esr spectrum of (a) 1,3-cyclo-
            octadiene semidione and   (b) 1,5-cyclooctadiene
            semidione prepared by addition of potassium
            t-butoxide and DMSO to a sample from the air
            oxidation of the monoepoxide in DMSO, catalyzed
            by boron trifluoride etherate.

(a)

0   10
GAUSS

(b)

0   5
GAUSS
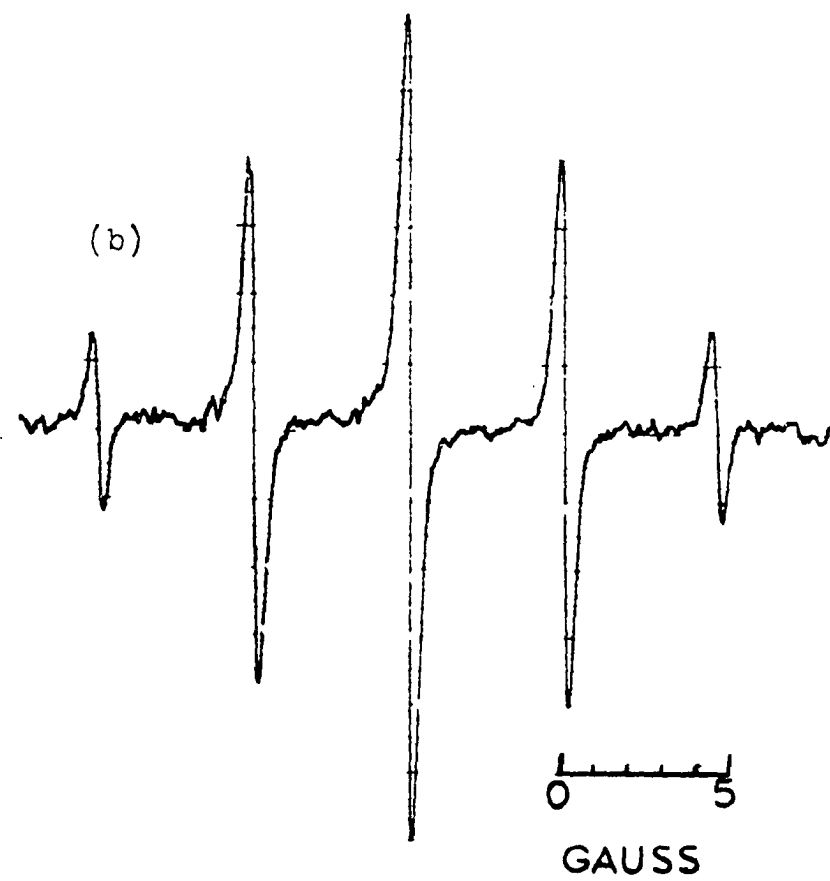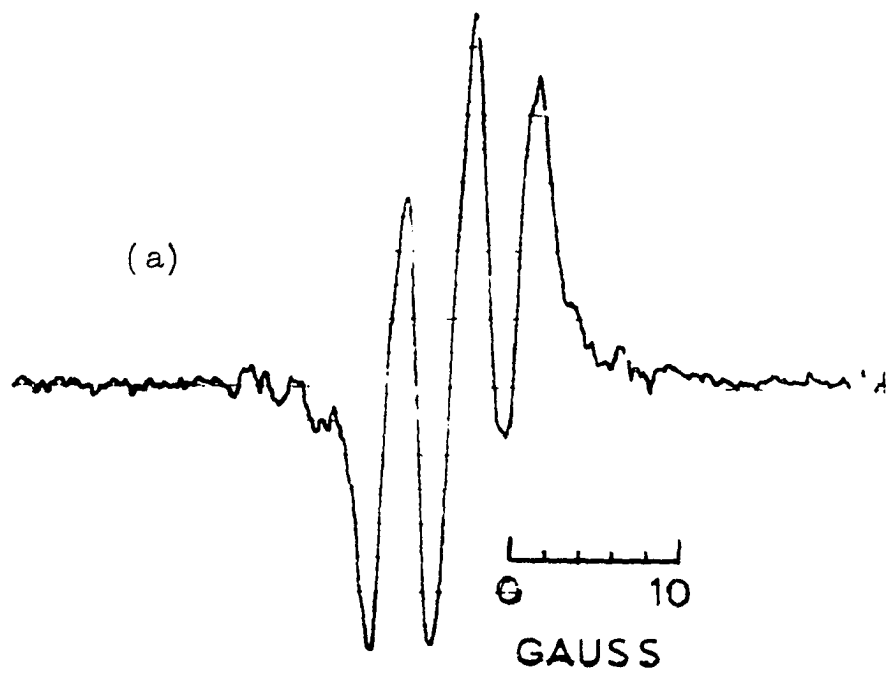
Figure 24a. First derivative esr spectrum of radical anion formed by reduction of dibenzo-[a,e]cyclooctatetraene-5,6-dione with propiophenone anion in potassium $\underline{t}$-butoxide-DMSO.

Figure 24b. Simulated spectrum for Lorentzian linewidth of 0.1 gauss and hfsc from the text performed by JEOLCO JNM-RA-1 spectrum accumulator.

(a)

(b)

GAUSS

1

0
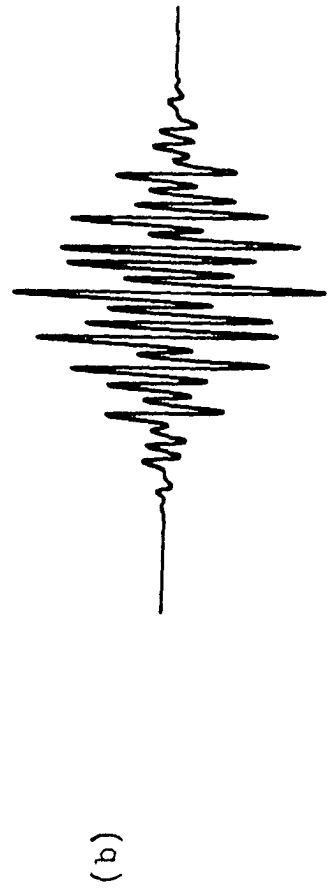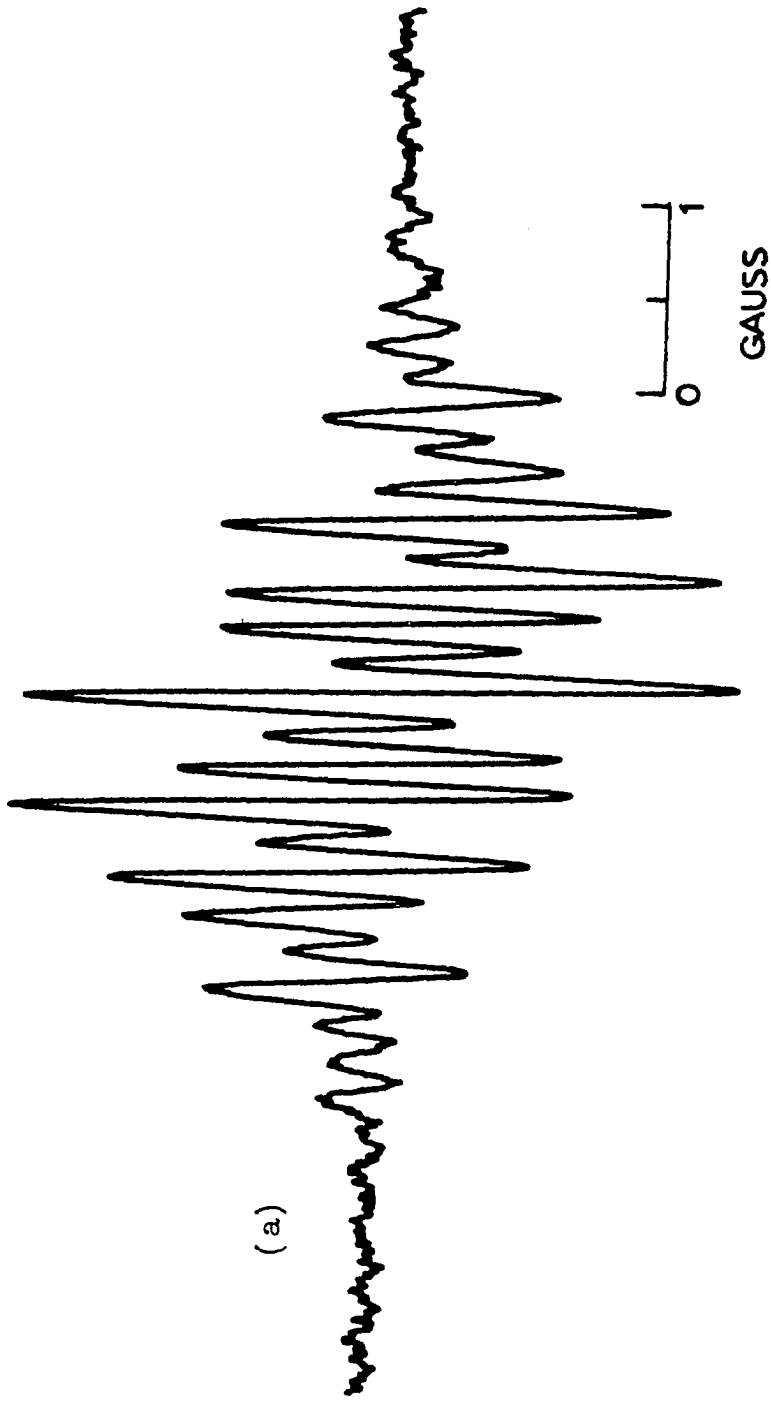
EXPERIMENTAL

All esr spectra were taken on Varian spectrometers, either model V4500 equipped with a nine inch magnet or model E3 equipped with a three inch magnet. Potassium and cesium t-butoxide were purchased from MSA Research Corporation and purified by sublimation when necessary. DMSO, from Crown Zellerback and from Baker, was distilled from calcium hydride and dried over molecular sieves.

Tetralones and o-Naphthoquinones

ESR sample preparation

The systems listed in Table 7 were used to generate the quinone and hydroxyquinone radical anions. Materials in side 1 and side 2 of the H cell were mixed and shaken down into the flat fused silica cell after degassing with prepurified nitrogen.

Materials used

Preparation of 7-methoxytetralone   β-(p-anisoyl)-propionic acid was prepared in 58% yield from reaction of anisole with succinic anhydride and aluminum chloride in 1-nitropropane, according to the method of Thomas and Nathan (48): mp 145-146°; ir (KBr) 1695, 1665, 1600 and 1575 cm^{-1}. The keto acid was reduced to γ-(p-anisyl)-butyric acid using the Huang-Minlon modification of the Wolff-Kishner reaction (49). A mixture of 54 g of the

Table 7. Systems used for generation of o-naphthosemiquinone radical ions.

Side 1	Side 2	Solvent	Time Degassed	Time Air Added
100 mg tetralone	10 mg potassium t-butoxide	1 ml DMSO	10 min	10 sec
2 mg quinone and 4 μl propiophenone	5 mg potassium t-butoxide	1 ml DSMO or 1 ml DMF	20 min	--
2 mg quinone and 3-4 mg zinc	0.1 ml 30% potassium hydroxide	1 ml DMF	20 min	--
5 mg quinone	5 mg sodium dithionite	1 ml 0.1 N potassium hydroxide	20 min	--
2 mg quinone	8 μl propiophenone	--	20 min	--
5 mg quinone and 5 μl propiophenone	8 mg potassium t-butoxide	1 ml t-butyl alcohol and 0.2 ml water	20 min	--

keto acid, 50 g potassium hydroxide and 35 ml hydrazine hydrate (85%, technical grade) in 350 ml diethylene glycol was heated to 110-120° in a 1 liter flask equipped with a Dean-Stark water separator. When no more water separated (about 3 hours) the temperature was raised to 190-200° and maintained there until no more nitrogen evolution could be detected (about 16 hours). The reaction mixture was cooled, diluted with 250 ml water and 250 ml 6N hydrochloric acid. The aqueous solution was extracted with four 300 ml portions of ether and the combined ether extracts washed with saturated salt solution, dried over magnesium sulfate and the ether removed on a rotary evaporator. The resulting oil in 200 ml 10% sodium hydroxide was heated with 50 g dimethyl sulfate at 90° for 2 hours with enough additional sodium hydroxide to insure alkalinity. The solution was then treated with charcoal and filtered hot, then cooled to 10° and slowly acidified. On filtration, 57 g of a white solid was isolated. This solid was dissolved in 5% sodium bicarbonate and the solution filtered to remove a residue, then slowly acidified. The solid which separated at this point was filtered and dried, yielding 38 g (76% yield) of white crystals: mp 60-61°; ir (KBr) 1690 and 1515 cm^{-1}.

This acid was cyclized to 7-methoxytetralone with phosphorus pentachloride and stannic chloride, again

following the general method of Thomas and Nathan (48).
A 20 g sample of the γ-(p-anisyl)butyric acid in 150 ml
benzene was stirred and cooled to 5°. To this was added
25 g phosphorus pentachloride at a rate to keep the
temperature below 10°. During this addition the color
changed to yellow-green. The mixture was then heated
at 50° for 15 minutes, cooled to 0°, and a precooled
solution of 20 ml fuming anhydrous stannic chloride in
20 ml benzene added rapidly with stirring. An initial
red color changed to dark green as the mixture solidified.
After standing at room temperature for one hour the
reaction mixture was hydrolyzed with 100 g ice, 100 ml
concentrated hydrochloric acid and 30 ml ether. The
solution was extracted with four 200 ml portions of ether,
and the combined ether extracts washed successively with
10% sodium hydroxide and saturated salt solution. The
sodium hydroxide caused a white precipitate to form
which was probably tin hydroxide. The ethereal solution
was filtered and dried over magnesium sulfate, and most
of the ether and benzene removed on a rotary evaporator.
The remainder was allowed to evaporate in air, and a pale
yellow solid formed which yielded 12.4 g (67% yield) white
crystals on recrystallization from benzene: mp 59-60°
(lit. mp 61-62.5° from petroleum ether); ir (CHCl₃) 1660
and 1600 cm⁻¹; nmr (CCl₄) δ 2.15 (m, 2), 2.4 (m, 2), 2.8

(t, 2), 3.75 (s, 3), 6.92 (m, 2) and 7.33 ppm (m, 1).

Preparation of the Wichelhaus Oxide (23, 24)   A
solution of 40 g of ferric chloride in 250 ml water was
added to 10 g of β-naphthoquinone in 200 ml water. The
mixture was stirred and heated at 60-70 until a yellow-
brown product suddenly settled out (30-40 minutes). The
mixture was cooled and filtered giving a yellow-brown
paste which was recrystallized according to Fieser's
procedure (25). The crude material was washed by stirring
in 300 ml portions of distilled water until the filtrate
was clear, showing removal of all excess ferric chloride.
About 5 g crude product was dissolved in 800 ml acetone
with 700 ml distilled water and 40 ml concentrated
hydrochloric acid. This mixture was allowed to stand
overnight and red-orange needles separated out which were
then filtered and dried, mp 256-259° (lit. mp 251-253°).

Conversion of 5-methoxytetralone to 5-methoxylawsone (7)
1 g 5-methoxytetralone and 2 g p-nitroso-N,N-dimethyl-
aniline were dissolved in 50 ml absolute ethanol with 1 ml
10% sodium hydroxide. After 2 hours a dark solid was
filtered from the solution and dried (d 167-168°). This
was presumably the dianil which was then hydrolyzed by
boiling in 50 ml 5% sulfuric acid. The crude solid
filtered from this solution gave the same esr spectrum
that was seen when the solution of 5-methoxytetralone

and potassium t-butoxide in DMSO with added oxygen was allowed to stand in the esr cell for 4-6 hours.

Synthesis of juglone (5-hydroxy-1,4-naphthoquinone) (50) Because of the questionable purity of the commercial juglone, material was synthesized for comparison of spectra. 50 g 1,5-dihydroxynaphthalene, 240 g sodium dichromate and 340 g sulfuric acid were added to 2 liters water at 0-5°. The mixture warmed rapidly and foamed excessively. A dark green solid was filtered from this solution and washed with several portions of Skelly B. Concentration of the washings yielded 2 g of orange crystals, purified by sublimation [mp 159-161° (lit. mp 149-150°)]. Spectra from this material were identical with those from the material purchased from Aldrich: nmr (CDCl$_3$)δ = 6.88 (s, 2), 7.24 (m, 1), 7.55 (m, 2) and 11.75 ppm (s, 1).

3-Benzosuberone-d$_4$ A 200 mg sample of the material synthesized by T. Ku was stirred overnight in 5 ml deutero-methanol containing a trace of sodium methoxide. After removal of solvent and drying, nmr analysis indicated more than 90% deuteration at the four α positions.

Cyclic Unsaturated Semidiones

ESR sample preparation

Attempts to form the semidiones of the unsaturated monoketones were carried out on 10-20 mg samples in 1 ml DMSO with 5-10 mg potassium t-butoxide. These solutions were degassed 10-15 minutes. Spectra of the degassed samples were run to check for spurious signals. Air was then admitted to the cells for 10-20 seconds, the samples were shaken, and the spectra rerun. In the case of the dibenzo-[a,e]-cyclooctatetraene-5,6-dione, 10 mg of the diketone, 4 µl propiophenone and 8 mg potassium t-butoxide in 1 ml DMSO was degassed twenty minutes.

Materials Used

Reduction of α-tropolone (32)   A 1 g sample of tropolone in 10 ml anhydrous ether was added slowly to a slurry of 200 mg lithium aluminum hydride in 30 ml ether. A yellow solid formed and persisted throughout an additional hour of refluxing. Excess hydride was decomposed with saturated ammonium sulfate solution. The ether layer was separated, the residue was extracted with additional ether, and the combined ethereal solutions dried over anhydrous sodium sulfate. Concentration gave a dark red oil, which mainly decomposed on distillation. 80 mg of a yellow oil (bpt 65-70°/7 mm) was collected but this yielded no

esr signal in DMSO with excess potassium t-butoxide or
potassium t-butoxide and propiophenone. Repeated attempts
at reduction gave the same red oil which defied distillation.

Preparation of 2,4-cycloheptadienone   3,5-diketo-
cyclohexanecarboxylic acid was prepared by Birch reduction
of 3,4,5-trimethoxybenzoic acid (51). A slurry of 53 g acid
in 375 ml ethanol was added slowly to 2.5 liters liquid
ammonia which had been condensed with dry ice-DMF. To
this solution was added 30 g sodium at a rate which main-
tained a steady reflux. The solution turned yellow after
the first few chunks had dissolved. The reaction was
allowed to stir for 15 minutes after all sodium was added,
then 125 g dry ammonium chloride was added. The condenser
was then removed, and the ammonia was evaporated with the
aid of an aspirator. The residue was dissolved in 500 ml
2 N hydrochloric acid and the resulting solution boiled
2-3 minutes. After cooling, the solution was extracted
with several portions of ether and dried over magnesium
sulfate. Evaporation of the ether gave a reddish-yellow
oil rather than the expected white crystals. A sample of
the oil dissolved in deuterochloroform for an nmr began
to form crystals after standing overnight, so chloroform
was added to the oil, and the mixture was refrigerated.
After about 24 hours the solution was filtered and yielded

16 grams white crystals, mp 177-180° (lit. 180°). The nmr
of the oil indicated the presence of ethoxy groups, and it
was presumed that partial esterification had occurred
during the boiling with acid, since ethanol was present
in the original reaction mixture. Since esterification
was the next step in the sequence, both oil and crystals
were used in the subsequent reaction. 3,5-Diketocyclo-
hexanecarboxylic acid was converted to the monoenol ether-
ester, bp 164-167° (5 mm); [lit. bp 125-130° (0.4 mm)];
ir (CCl₄) 1725, 1650 and 1600 cm⁻¹; nmr (CCl₄) δ 1.25
(t, 2), 1.40 (t, 2), 2.5 (m, 4), 3.0 (m, 1), 3.95 (q, 2),
4.12 (q, 2) and 5.25 ppm (s, 1). This compound was reduced
with lithium aluminum hydride to 5-hydroxymethyl-2-cyclo-
hexenone ir (CHCl₃) 3400 and 1670 cm⁻¹ according to
van Tamelen's procedure (33). 5-Hydroxymethyl-2-cyclo-
hexenone tosylate was prepared from the crude alcohol
using the general procedure of Tipson (52). The oil
which had been obtained from reduction of 16 g of ester
was used without further purification since it reportedly
could not be distilled (33). The oil in 100 ml dry
pyridine was cooled to -5° in ice salt and 13.2 g dry
toluenesulfonyl chloride was added in one portion. The
flask was stoppered and swirled until all the chloride
had dissolved. After standing at 0° overnight, the
reaction was worked up and the product isolated following

van Tamelen's procedure. Recrystallization from 95% ethanol

gave 6.5 g of white needles: mp 74-75° (lit. mp 75.0-75.7°);

nmr (CDCl₃) δ 2.32, 2.45 (m, 7 or 8), 4.0 (d, 2), 6.02

(m, 1), 6.95 (m, 1), 7.35 (d, 2) and 7.8 ppm (d, 2).

2,4-cycloheptadienone was prepared by solvolysis of the

tosylate in aqueous sodium hydroxide and ether using

van Tamelen's procedure. The dark red oil obtained from

6 g tosylate was distilled, yielding 1.5 grams of yellow

liquid: bp 65-66° (4 mm) [lit. bp 39-42° (0.5 mm)];

ir (CHCl₃) 1655 cm⁻¹; nmr (CDCl₃) δ 2.55 (m, 4) and 6.35

ppm (m, 4).

Preparation of cyclooctene semidiones   1,3-Cyclo-

octadiene monoepoxide was prepared according to Cope's

procedure with peracetic acid (36). Addition of 110 g

of 40% peracetic acid solution to 46 g of 1,3-cycloocta-

diene required 2 hours, keeping the temperature below

35°. The initial fraction from distillation of the product

identified as the monoepoxide was 24 g of a liquid: bp

83-88° (22 mm) ir (CCl₄). A second fraction [bp 120-125°

(10 mm)] was not characterized. 1,5-Cyclooctadiene

monoepoxide was prepared in the same way from 10 g

of diene with 25 g peracetic acid solution added during

one hour. This yielded 6 g of colorless liquid: bp

82-86° (23 mm); ir (CCl₄) nmr (CCl₄) δ 2.0 (m, 8), 2.85

(m, 2) and 5.55 ppm (m, 2). A higher boiling fraction

was again noted [bp 115-119° (15 mm)].

Conversion of the epoxides to hydroxy ketones was effected by Cohen and Tsuji's method of oxidation in DMSO (35). A 5 g sample of the 1,3-cyclooctadiene monoepoxide in 12 ml DMSO with one drop boron trifluoride etherate was stirred in air in an oil bath at 80° for 10 hours. A 0.5 ml sample of the mixture removed at that time gave an esr signal in additional DMSO with potassium t-butoxide. A 3 g sample of the 1,5-cyclooctadiene monoepoxide in 10 ml DMSO with one drop boron trifluoride etherate was stirred in air at 60-70° for 24 hours. A sample removed at that time gave no esr signal. The mixture was allowed to stir at 70° with an additional drop of boron trifluoride etherate for 60 hours longer. An 0.5 ml sample removed at this time gave a strong esr signal in added DMSO and potassium t-butoxide. Another reaction at 90-105° for 48 hours also resulted in material which gave an esr signal.

Attempts to isolate the hydroxyketones were unsuccessful. When unreacted epoxide and DMSO were distilled away, only a few drops of a dark residue remained, which still gave a strong esr signal. An ir spectrum of the residue showed absorptions at 3400 and 1700 cm^{-1} not present in the starting materials. The nmr showed a new broad absorption due to one proton, possibly an O-H or

-C<u>H</u>OH at 4.1 ppm, and additional methylene absorptions at 2.9 ppm, probably due to -CH$_2$-CO resonance.

Mystery Radical from Cycloheptatriene

<u>ESR sample preparation</u>

The following proportions are approximately those needed to observe the radical from cycloheptatriene: 25 μl cycloheptatriene, 120 mg potassium <u>t</u>-butoxide and 1 ml DMSO. The cycloheptatriene in one leg of the esr cell, and the base-DMSO in the other, were degassed twenty minutes. On mixing, a deep purple color developed in all cases where a radical was observed. If lower concentrations or a smaller excess of base was used, the solution on mixing was yellow or brown and no radical was seen. The purple color, and the esr signal, persisted for several hours unless air was added, in which case the signal was destroyed immediately.

The sample could be quenched by injecting 20-30 ul water through the rubber septum before opening the cell to air. This solution was then poured into additional water, and extracted with two or three 10 ml portions of ether. The ether was evaporated and a mass spectrum taken of the residue. No significant peaks other than those attributable to starting materials were observed.

When 1 ml dimethylformamide or hexamethylphosphoramide was substituted for DMSO as solvent, no radical was

observed.

About 50 mg of a sodium hydride-oil dispersion was added under nitrogen to 1 ml DMSO which had been degassed 10 minutes, in one leg of the esr cell. The other leg contained 20 ml cycloheptatriene. After an additional 10 minutes degassing, the cell was stoppered and the cycloheptatriene mixed with the hydride-DMSO. The cell was allowed to stand two to four hours until most of the hydride had dissolved and the solution was deep purple. This was then shaken down into the flat cell and the spectrum taken. No radical was seen.

A 1:1 mixture of sodium and potassium in dimethoxy-ethane was also used in place of the $\underline{t}$-butoxide and DMSO. Again a deep purple color developed in the solution, but no radical was seen.

10 mg of the 5-hydroxymethyl-2-cyclohexenonetosylate from the 2,4-cycloheptadienone synthesis was tested with 5 mg and with 25 mg of potassium $\underline{t}$-butoxide in 1 ml DMSO. Neither case produced a radical, with or without air added to the sample. Another 10 mg sample in 1 ml of 0.1 N potassium hydroxide also failed to give any esr signal, with or without added air. The dienone itself also gave negative results under all of these conditions.

Materials used

Cycloheptatriene, from Shell and Aldrich, was passed
through silica gel and then distilled on a Todd column
(bp 114-115°). The center cut still contained 3-4%
toluene and 1% norbornadiene by glpc. This material
was collected successively from glpc with an ODPN column
at 80°, which separated the norbornadiene and an SF 96
column at 90° which separated most of the toluene.

Synthesis of DMSO via trimethylsulfoxonium iodide

A solution of 16 g dry distilled DMSO and 30 ml methyl
iodide was refluxed for 3 days. The solid which had
separated was filtered and washed with chloroform. This
crude yellow salt was recrystallized from water to give
pure white needles (53). The salt was decomposed to DMSO
by the method of Cotton (54), by heating a flask with a
short distilling head for about 2 hours at 200° and 20 mm.
The yellow distillate was warmed with thiosulfate, then
distilled from barium oxide and dried over molecular
sieves: bp 85-87° (25 mm).

Substituted Cycloheptatrienes

Synthetic cycloheptatriene, 7-deutereocycloheptatriene
and 7-phenylcycloheptatriene were obtained from M. Dwight
Robbins. 7-methoxy-, 7-methyl-, 7-ethyl- and 7-isopropyl-
cycloheptatriene were prepared by the author. All were
made from tropylium tetrafluoroborate, by reacting it

with sodium borohydride, sodium borodeuteride, phenyl or alkylmagnesium halides or methanol. The tetrafluoroborate was made by Dauben's in situ technique, from commerical triphenylcarbinol (55). Yields of the alkyl substituted cycloheptatrienes were generally poor, owing chiefly to the difficulties encountered in distillation, especially that of excessive foaming. The 7-methoxy compound was made according to Conrow's procedure for the ethoxy-compound (56). From 10 g tetrafluoroborate in 30 ml methanol and 60 ml water, with excess sodium bicarbonate, 8 ml of clear, colorless liquid was obtained, bp 55-57° 9 mm.

3,7,7-trimethylcycloheptatriene was prepared by lithium aluminum hydride reduction of encarvone, followed by dehydration of the resultant alcohol by distillation from potassium hydrogen sulfate, by the procedure of Jones and Jones and references cited by them (57).

Isomerization of cycloheptatrienes

Isomerization of the cycloheptatrienes is easily monitored by nmr. The 7-phenyl-compound was converted to the 3-phenyl- by placing 200 mg of material in a sealed tube in refluxing xylene for 3 hours. A 1/2 ml sample of the 7-methoxy compound was placed for one hour in refluxing xylene in a sealed tube. At the end of the

hour, nmr indicated about 40% conversion to 3-methoxycyclo-
heptatriene. A new sample was then placed in an oil bath
at 150° for two hours. An nmr spectrum of the material
at this time showed complete conversion of the 7- to
about 90% of 3- and 10% of 1-methoxycycloheptatriene (53).
The nmr spectrum of the 7-methoxycompound shows absorptions
due to the 7-proton at 3.2 ppm (m) and the methoxy protons
at 3.32 ppm (s). In the spectrum of the 3-methoxycyclo-
heptatriene the methoxy shifts to 3.56 ppm, and the triplet
due to the two 7-protons appears at 2.2 ppm. In the
1-methoxy compound the methoxy protons absorb at 3.5 ppm,
and there is a doublet from the 7-protons at 2.45.

Photoisomerization of cycloheptatriene to bicyclo-[3.2.2]-
hepta-2,5-diene (44)   A solution of 13 g freshly
distilled cycloheptatriene in 700 ml dry ether was irradiated
under reflux in a Rayonet Srinivasan-Griffin photochemical
reactor with 2537 Å Hg lamps for 11 1/2 days. At this
time most of the ether was removed on a rotary evaporator
and the remainder distilled at atmospheric pressure. A
4 ml sample liquid boiling up to 100° was collected. Nmr
and glpc indicated this to be approximately equal amounts
of two components, one of which was unreacted cyclohepta-
triene. The other isomer was collected by glpc from a 15%
Carbowax 20M column at 55°, detector temperature 105°.
Its nmr spectrum was identical with that reported in the

literature for the bicyclo[3.2.0]hepta-2,5-diene: δ (CCl_4)

2.33, 3.27, 3.62 and 5.64 ppm, all broad multiplets and

doublets at 6.08 and 6.33 ppm.

Attempted preparation of bicyclo 5.1.0 octadienes

The procedure of Le Goff (59) for preparing the Zn/Cu

couple for the Simmons-Smith reagent was followed, and

the reaction done on 25 g cycloheptatriene with 0.5 moles

couple. After concentration of the product ether solution,

glpc on a Carbowax 20 M column at 130° gave six product

peaks in addition to unreacted cycloheptatriene. The

mixture was distilled in an attempt to remove the latter,

and this resulted in a change in the relative amounts of

the first two product peaks. Enough of these was collected

for esr spectra. Product A gave no signal with excess

potassium t-butoxide and DMSO; product B gave a weak but

growing signal identical to that from cyclooctatetraene.

Phenylcycloheptatriene radical anions   Samples of

20 mg of either 3- or 7-phenylcycloheptatriene with 100 mg

potassium t-butoxide in 1 ml DMSO gave deep purple solutions

which gave identical esr signals.

The samples were quenched with deuterium oxide in the

esr cells and extracted with three portions of ether. The

ether solution was washed with three portions of water,

dried over magnesium sulfate, and the ether evaporated.

Nmr spectra of the residues showed absorption only in the

phenyl region as a broad multiplet from 7.0 to 7.6 ppm.[a]
No cycloheptatriene peaks remained. Glpc of the starting
material on a QF column indicated the presence of 2-3%
biphenyl as identified by peak enhancement with authentic
material. Mass spectra of the esr sample residues
indicated a much larger amount of material with m/e 154,
the molecular weight of biphenyl, than was present in the
starting material.

Table 8. Mass spectral data for phenylcycloheptatriene esr
sample residues

	m/e	Relative Intensity
Starting 3-phenylcycloheptatriene	154	52
	168 (M)	204
	169	25
	170	2
Residue from esr sample quenched with D_2O	154	40
	168	2
	169	0.5
	170	0.2

[a]This absorption is similar to that shown by biphenyl.
See the Varian catalog, No. 289.

LITERATURE CITED

1. Russell, G. A. and E. T. Strom, J. Amer. Chem. Soc., 86, 744 (1964).

2. Russell, G. A., G. A. Underwood and D. C. Lini, J. Amer. Chem. Soc., 89, 6636 (1967).

3. Talaty, E. R. and G. A. Russell, J. Amer. Chem. Soc., 87, 4867 (1965).

4. Russell, G. A. and K. Y. Chang, J. Amer. Chem. Soc., 87, 4381 (1965).

5. Baillie, A. C. and R. H. Thomson, J. Chem. Soc., C, 2184 (1966).

6. Kasturi, T. R. and T. Arunachalam, Can. J. Chem., 44, 1086 (1966).

7. Buu-Hoi, MM. and P. Cagniant, Compt. rend., 214, 87 (1942); Cooke, R. G. and W. Segal, Aust. J. Sci. Res., 3A, 628 (1950).

8. Adams, M., M. S. Blois, Jr. and R. H. Sands, J. Chem. Phys., 28, 774 (1958).

9. Kuboyama, A., Bull. Chem. Soc. Jap., 32, 1226 (1959).

10. Vincow, G. and G. K. Fraenkel, J. Chem. Phys., 34, 1333 (1961).

11. Dehl, R. and G. K. Fraenkel, J. Chem. Phys., 39, 1793 (1963).

12. Bersohn, R., J. Chem. Phys., 24, 1066 (1956).

13. Brandon, R. W. and E. A. C. Lucken, J. Chem. Soc., 4273 (1961).

14. Stone, T. J. and W. A. Waters, J. Chem. Soc., 1488 (1965).

15. Thomson, R. H., Naturally Occurring Quinones, New York, N.Y., Academic Press, Inc. 1957.

16. Radt, F., ed., Elsevier's Encyclopedia of Organic Chemistry, Series III, Volume 12B, New York, N.Y., Elsevier Publishing Co. 1952.

17. Fieser, L. F., W. P. Campbell and E. M. Foy, J. Amer. Chem. Soc., 61, 2206 (1939).

18. Fieser, L. F., J. P. Shirmer, S. Archer, R. R. Lorenz and P. I. Pfaffenbach, J. Med. Chem., 10, 513 (1967); Fieser, L. F., M. Z. Nazer, S. Archer, D. A. Berberian and R. G. Slighter, J. Med. Chem., 10, 517 (1967), and references cited therein.

19. Stone, E. W. and A. H. Maki, J. Chem. Phys., 36, 1944 (1962).

20. Gendell, J., J. H. Freed and G. K. Fraenkel, J. Chem. Phys., 37, 2832 (1962).

21. Hollocher, T. C. and M. M. Weber, Nature, 195, 247 (1962); Hollocher, T. C., N. M. Tooney and R. Adman, Nature, 197, 74 (1963).

22. Piette, L. H., M. Okamura, G. P. Rabold, R. T. Ogata, R. E. Moore and P. J. Scheuer, J. Phys. Chem., 71, 29 (1967); Rabold, G. P., R. T. Ogata, M. Okamura, L. H. Piette, R. E. Moore and P. J. Scheuer, J. Chem. Phys., 46, 1161 (1967).

23. Wichelhaus, H., Chem. Ber., 30, 2199 (1897).

24. Hooker, S. C. and L. F. Fieser, J. Amer. Chem. Soc., 58, 1216 (1936); Hooker, S. C., J. Amer. Chem. Soc., 58, 1163, 1168, 1174, 1181, 1190, 1212 (1936); Hooker, S. C. and A. Steyermark, J. Amer. Chem. Soc., 58, 1179, 1198, 1202, 1207 (1936).

25. Fieser, L. F. and D. H. Sachs, J. Amer. Chem. Soc., 90, 4129 (1968).

26. Wanzlick, H. -W., M. Lehmann-Horchler and S. Mohrmann, Chem. Ber., 90, 2521 (1957).

27. Weiner, S. A., Generation of Semidione and Semitrione Radical Anions in Dimethyl Sulfoxide. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1967.

28. Schroder, G., Chem. Ber., 97, 3140 (1964); Doering, W. von E. and J. W. Rosenthal, J. Amer. Chem. Soc., 88, 2078 (1966).

29. Jones, M. Jr., J. Amer. Chem. Soc., 89, 4236 (1967).

30. Russell, G. A., E. T. Strom, E. R. Talaty and S. A. Weiner, J. Amer. Chem. Soc., 88, 1998 (1966).

31. Myers, C. L. Aromatic and Heterocyclic Semidiones. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1968.

32. Cook, J. W., R. A. Raphael and A. I. Scott, J. Chem. Soc., 4416 (1952).

33. van Tamelen, E. E. and G. T. Hildahl, J. Amer. Chem. Soc., 78, 4405 (1956).

34. Russell, G. A. and P. R. Whittle, J. Amer. Chem. Soc., 89, 6781 (1967); Malkus, H. L., Conformational Studies of Acyclic Semidiones. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1968.

35. Cohen, T. and T. Tsuji, J. Org. Chem., 26, 1681 (1961); T. Tsuji, Tetrahedron Lett., 2413 (1966).

36. Cope, A. C. and P. E. Peterson, J. Amer. Chem. Soc., 81, 1643 (1959).

37. Cope, A. C., S. F. Schaeren and E. R. Trumbull, J. Amer. Chem. Soc., 76, 1096 (1954); Cope, A. C. and B. D. Tiffany, J. Amer. Chem. Soc., 73, 4158 (1951).

38. Hall, T. K., Chemical and Photochemical Studies of Unsaturated Cyclooctane Derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1967.

39. Burns, M. E., Dissertation Abstracts, 28, 1412B (1967).

40. Levy, D. H. and R. J. Myers, J. Chem. Phys., 43, 3063 (1965).

41. Bauld, N. L. and M. S. Brown, J. Amer. Chem. Soc., 87, 4390 (1965).

42. Strauss, H. L., T. J. Katz and G. K. Fraenkel, J. Amer. Chem. Soc., 85, 2360 (1963).

43. Dauben, H. J. and M. R. Rifi, J. Amer. Chem. Soc., 85, 3041 (1963).

44. Dauben, W. G. and R. L. Cargill, Tetrahedron, 12, 186 (1961).

45. Corey, E. J. and M. Chaykovsky, J. Amer. Chem. Soc., 87, 1353 (1965).

46. Doering, W. von E. and W. R. Roth, Tetrahedron, 19, 715 (1963).

47. van Tamelen, E. E., J. McNary, and F. A. Lornitzo, J. Amer. Chem. Soc., 79, 1231 (1957).

48. Thomas, D. G. and A. H. Nathan, J. Amer. Chem. Soc., 70, 331 (1948).

49. Minlon, H., J. Amer. Chem. Soc., 68, 2487 (1946).

50. Willstatter, R. and A. S. Wheeler, Chem.-Ber., 47, 2796 (1914); Fieser, L. F. and J. T. Dunn, J. Amer. Chem. Soc., 59, 1016 (1937).

51. Birch, A. J., P. Hextall and S. Sternhell, Aust. J. Chem., 7, 256 (1954).

52. Tipson, R. S., J. Org. Chem., 9, 235 (1944).

53. Kuhn, R. and H. Trischmann, Ann. Chem., 611, 117 (1958).

54. Cotton, F. A., J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, J. Chem. Soc., 4138 (1959).

55. Dauben, H. J., Jr., L. R. Honnen and K. M. Harmon, J. Org. Chem., 25, 1442 (1960).

56. Conrow, K., J. Amer. Chem. Soc., 83, 2343 (1961).

57. Jones, L. B. and V. K. Jones, J. Amer. Chem. Soc., 89, 1880 (1967).

58. Weth, E. and A. S. Dreiding, Proc. Chem. Soc., 59 (1964).

59. LeGoff, E., J. Org. Chem., 29, 2048 (1964).

ACKNOWLEDGMENTS